

11th Annual European Rheology Conference

26th Nordic Rheology Conference



April 3 – 6, 2017 Copenhagen, Denmark



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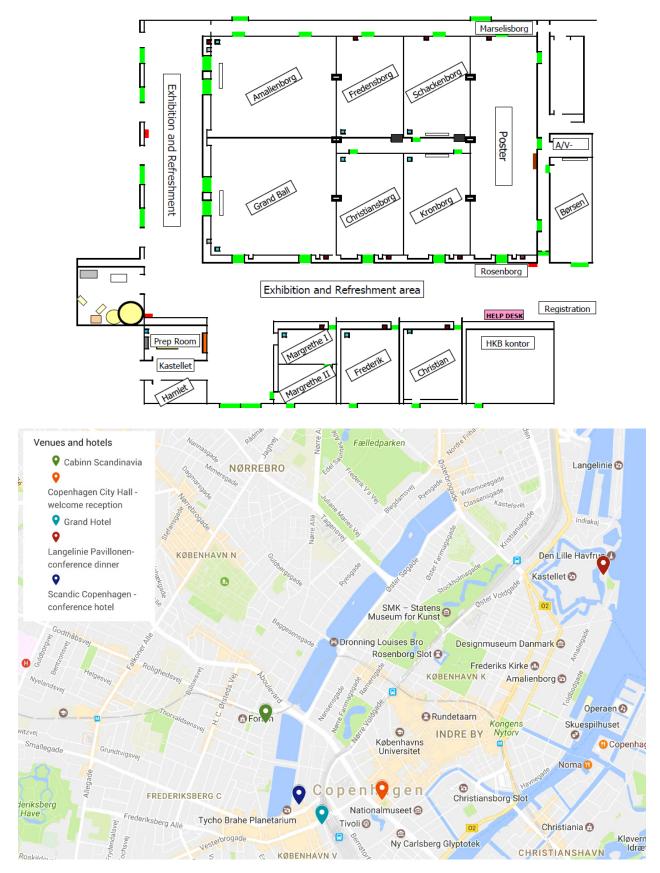
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Conference Venue & Floor Plan

Scandic Copenhagen Hotel, Vester Søgade 6, 1601 Copenhagen V, Denmark



Welcome to AERC 2017 in Copenhagen

Welcome to the 11th Annual European Rheology Conference in Copenhagen! Organized by the Nordic Rheology Society, this international conference is also the 26th Nordic Rheology Conference. The conference features 4 plenary lectures including the Weissenberg presentation. With more than 400 accepted contributions (oral and posters) from 37 countries it promises to continue the line of successful European rheology conferences. A special welcome goes to the many overseas delegates. With 25% of the contributions from outside Europe, the AERC meetings are increasingly becoming an occasion for exchange of ideas and friendships



on the international level. Additionally, twelve companies and associations have chosen this meeting to display their activities including the latest developments in rheological instrumentation.

Many institutions and persons have contributed to making all this possible. First of all thank you to the European Society of Rheology for giving us the opportunity to host the AERC 2017. We are truly grateful for this rheological platform. Thank you also to the scientific chair persons who have organized the nine sessions. Eleven companies and organizations have sponsored the meeting either directly or in connection with specific events. Their generous support is gratefully acknowledged. Without that support, the meeting would not have been possible. International colleagues have provided ideas and moral support. Local colleagues and students have provided hard work at long hours. All this is gratefully acknowledged.

I would like to close with a historical background on the city in which you are now located. The first written mention of Copenhagen may be found in the Icelandic Knytlingesaga. There it is stated that Svend Eskildsen (Svend, son of Eskild) in 1024 established his home base in "Havn" after having been defeated by Magnus den Gode (Magnus the good). "Havn" means simply harbor and referred to a small fishing village located approximately where the center of Copenhagen is today. In the middle ages, Havn grew in importance as a hub for fishing and trading and acquired its current name "København", the merchants harbor. In Latin, however, Copenhagen has retained its original name Hafnia. This is reflected in naming of the element hafnium (Hf⁷²) discovered in 1923 at the Niels Bohr institute at Copenhagen University.

Today, Copenhagen has grown to cover a large part of the island of Sjælland (Sealand). The Copenhagen Metropolitan area in Denmark has more than 2 million inhabitants. Connected by bridge to southern Sweden, the region has become an internationally recognized science center with a high density of universities, hospitals, knowledge institutions, as well as research and development based organizations.

On behalf of the organizing committee, it is my privilege to welcome you all to the city that has given its name to an element in the periodic table. Be assured that we will make every effort to make the AERC 2017 Copenhagen an outstanding and memorable success.

On behalf of the AERC2017 organizing committee,

la Herry

Ole Hassager

Organizing Committee

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Scientific Sessions and Chair Persons

Suspensions and colloids

Norbert Willenbacher *Karlsruhe Institute of Technology* Philippe Coussot *Université Paris-Est, ParisTech*

Non-Newtonian fluid mechanics and fluid instabilities

Natalie Germann Technical University of Munich Suzanne Fielding Durham University

Solids, glasses, and composites

Jeppe C. Dyre *Roskilde Universitet, Denmark* Esmaeil Narimissa *Technische Universität Berlin*

Food and biorheology

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Micro and nanorheology, microfluidics

Eric M. Furst University of Delaware Anke Lindner Université Paris Diderot, ESPCI Paris

• Polymer solutions and melts

Giovanni Ianniruberto Università degli Studi di Napoli Federico II Qian Huang Technical University of Denmark

Rheology of powders and granular material

Changquan Calvin Sun University of Minnesota Dietmar Schulze Ostfalia University of Applied Science

Gels and self-assembled systems

Moshe Gottlieb *Ben-Gurion University of the Negev* Henning H. Winter *University of Massachusetts Amherst*

Interfacial rheology

Natalie Medlicott University of Otago Peter Fischer ETH Zurich

Program Overview – Day 1

Apr.4, Tuesday	Track 1	Track 2	Track 3	Track 4	Track 5	Track 6	
	Grand Ball	Amalienborg	Christiansborg	Fredensborg	Kronborg	Schackenborg	
08:30-09:00	Opening (Grand Ball Complex)						
09:00-10:00	Weissenberg Awardee Talk - Philippe Coussot (Grand Ball Complex)						
10:00-10:30	Coffee Break						
10:30-10:50	SC1-Keynote-	NF1-Baumberger	SM1-Tassieri	FB1-Engmann	SG1-Marcourt	GS1-Dijkstra	
10:50-11:10	Willenbacher	NF2-Bechert	SM2-Edinger	FB2-Surber	SG2-Auhl	GS2-Carrot	
11:10-11:30	SC2-Gury	NF3- Chatzigiannakis	SM3-Laukkanen	FB3-Lupi	SG3-Keynote-Choi	GS3-Larsson	
11:30-11:50	SC3-Crassous	NF4-Allal	SM4-Boukany	FB4-Baldino		GS4-Lee	
11:50-12:10	SC4- Malkin	NF5-Kádár	SM5-Kulichikhin	FB5-Keynote-	SG4-Filip	GS5-Brem	
12:10-12:30	SC5-Parisi	NF6-Giacomin	SM6-Song	Gunes	SG5-Hoseini	GS6-Stadler	
12:30-13:30		Lunch					
13:30-13:50	SC6-Maia	NF7-Porcar	SM7-Matsumiya	FB6-Karlsson	SG6-Kim	GS7 - Keynote-	
13:50-14:10	SC7-Mattiello	NF8-Hemingway	SM8-Wagner	FB7-Turcanu	SG7-El Kissi	Richtering	
14:10-14:30	SC8-Swan	NF9-Jin	SM9-Ianniruberto	FB8-Yazar	SG8-Andrade	GS8-Hendricks	
14:30-14:50	SC9-Petekidis	NF10-Germann	SM10-Coppola	FB9-Buldo	SG9-Beuguel	GS9-Cloitre	
14:50-15:10	SC10-Schroyen	NF11-Caton	SM11-Taghipour	FB10-Stading	SG10-Stephanou	GS10-Cohen- Addad	
15:10-15:30	SC11-Zia	NF12-Fielding	SM12-Varchanis	FB11- Khosrowshahi	SG11-Kracalik	GS11-Winter	
15:30-16:00	Coffee Break						
16:00-16:20	SC12-Schweizer	NF13-Webster	SM13-Deplancke	FB12-Meerts	SG12-Hecksher	GS12-McKinley	
16:20-16:40	SC13-Zhang	NF14 -Keynote -	SM14-Martins	FB13-Pedersen	SG13-Ingebrigtsen	GS13-Goldansaz	
16:40-17:00	SC14-Schmid	Ramos	SM15-Handge	FB14-Berta	SG14-Shin	GS14-Inoue	
17:00-17:20	SC15-Wyss	NF15-Casanellas	SM16-Liu	FB15-Roux	SG15-Laukkanen	GS15-Pasquino	
17:20-17:40	SC16-Hallez	NF16- Mompean	SM17-Vervoort	FB16-Ramaioli	SG16-Keynote-	GS16-Louhichi	
17:40-18:00	SC17-Peters	NF17-Balan	SM18-Lu	FB17-Deshmukh	Voigtmann	GS17-Zhuge	
18:00-20:00	Poster Session 1 (Marselisborg & Rosenborg) / ESR committee meeting (Christiansborg)						

SC=Suspensions & Colloids; NF=Non-Newtonian fluid & Fluid instabilities; SM=Polymer Solutions & Melts; FB=Food & Biorheology; SG=Solids, Glasses & Composites; GS=Gels and Self-assembled systems

Program Overview – Day 2 & 3

Apr.5, Wednesday	Track 1	Track 2	Track 3	Track 4	Track 5	Track 6
	Grand Ball	Amalienborg	Christiansborg	Fredensborg	Kronborg	Schackenborg
08:30-09:30	Plenary talk - Jason Stokes (Grand Ball Complex)					
09:30-10:00	Coffee Break					
10:00-10:20	SC18-Domurath	NF18-Cruz	SM19- Keynote-	FB18-Arnfast	SG17-Marek	MN1-Georgiev
10:20-10:40	SC19-Gallier	NF19-Haward	Vlassopoulos	FB19-Helleberg	SG18-Lee	MN2-Maitri
10:40-11:00	SC20-Mehrdad	NF20-Formenti	SM20-Doi	FB20-Rühs	SG19-Zakhari	MN3-Trofa
11:00-11:20	SC21-Ausias	NF21-Clasen	SM21-Watanabe	FB21-Swan	SG20-Haldenwang	MN4-Pettas
11:20-11:40	SC22-Alghalibi	NF22-Verbeke	SM22-Chen	FB22-Fedosov	SG21-Galindo- Rosales	MN5-Caserta
11:40-12:00	SC23-Abbas	NF23-Poole	SM23-Plog	FB23-Windberger	SG22-Kaschta	MN6-Reichert
12:00-13:00		Lui	nch / NRS Annual Me	eting (Christiansbo	rg)	
13:00-13:20	SC24-Järnström	NF24- Patrascu	SM24-Wingstrand	FB24-Pokki	PG1-Amon	MN7 - Keynote-
13:20-13:40	SC25-Yüce	NF25-de Souza Mendes	SM25-Alvares	FB25-Wagner	PG2-Petersen	Schroeder
13:40-14:00	SC26-Liberto	NF26-Minale	SM26-Räntzsch	FB26-Keynote-	PG3-Gstöhl	MN8-Cardinaels
14:00-14:20	SC27-Volkova	NF27-De	SM27-Kempf	Sekulovic	PG4-Bek	MN9-Fidalgo
14:20-15:50	Poster Session 2 (Marselisborg & Rosenborg) / Coffee Break					
15:50-16:10	SC28 - Keynote-	NF28-Grizzuti	SM28-Doelder	IR1-Fuller	PG5-Fall	MN10-Fischer
16:10-16:30	Morris	NF29-Zhou	SM29-Stephanou	IR2-de Loubens	PG6-Trulsson	MN11-Preziosi
16:30-16:50	SC29-Colin	NF30-Frigaard	SM30-Abbasi	IR3-Jorgensen	PG7-Denis	MN12-Giudice
16:50-17:10	SC30-Comtet	NF31-Naccache	SM31-Yan	IR4-Guerrero	PG8-Goddard	MN13-Shen
17:10-17:30	SC31-Goharpey	NF32-Chaparian	SM32-Kruse	IR5-van Ammel	PG9-Keynote-	MN14-Padding
17:30-17:50	SC32-Dong	NF33-Nouar	SM33-Auhl	IR6-Rehage	Lumay	MN15-Caiazza
18:40-21:00	Conference Dinner					

SC=Suspensions & Colloids; NF=Non-Newtonian fluid & Fluid instabilities; SM=Polymer Solutions & Melts; FB=Food & Biorheology; SG=Solids, Glasses & Composites; IR=Interfacial Rheology; PG=Powders and Granular material; MN=Micro & Nanorheology, Microfluidics

Apr.6, Thursday	Track 1	Track 2	Track 3	Track 4	Track 5	Track 6	
	Grand Ball	Amalienborg	Christiansborg	Fredensborg	Kronborg	Schackenborg	
08:30-09:00	Awards (Grand Ball Complex)						
09:00-10:00	Plenary talk - Evelyne van Ruymbeke (Grand Ball Complex)						
10:00-10:30		Coffee Break					
10:30-10:50	SC33-Ito	NF34-Sucena	GS18-Martinoty	IR7-Keynote-	PG10-da Silva	MN16-Barentin	
10:50-11:10	SC34-Lang	NF35-D'Avino	GS19-Mao	Vermant	PG11-Curto	MN17-de Corato	
11:10-11:30	SC35-Gamonpilas	NF36-Ingelsten	GS20-Natalia	IR8-Pepicelli	PG12-Seguin	MN18-Schmidt	
11:30-11:50	SC36-Ovarlez	NF37-Cardenas	GS21-Aime	IR9-Gottlieb	PG13-Mahajan	MN19-Adamska	
11:50-12:10	SC37-Korculanin	NF38-Prieto	GS22-Maia	IR10-Walker	PG14-Valette	MN20-Furst	
12:10-12:30	SC38-Cidade	NF39-Castellani	GS23-Colombo	IR11-Tajuelo	PG15-Puyvelde	MN21-Reufer	
12:30-13:30	Lunch						
13:30-14:30	Plenary talk - Sandra Lerouge (Grand Ball Complex)						
14:30-15:00	Coffee Break						
15:00-15:20	SC39-Kuzhir	NF40-Negrao	GS24-Dessi	IR12-Jullien	PG16-Ferri	MN22-	
						Aangenendt	
15:20-15:40	SC40-Vazquez-		CC2E Comunati		PG17-Hirschberg	MNI22 Cartina	
	Quesada	NF41-Marchesini	GS25-Caruggi	IR13-Vitasari		MN23-Garting	
15:40-16:00	SC41-Laure	NF42-Varé	GS26-Hesarinejad	IR14-Xu		MN24-Lanzaro	
16:00-16:30		Closing (Grand Ball)					

SC=Suspensions & Colloids; NF=Non-Newtonian fluid & Fluid instabilities; GS=Gels and Self-assembled systems

IR=Interfacial Rheology; PG=Powders and Granular material; MN=Micro & Nanorheology, Microfluidics

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Tuesday Morning

Symposium PL

Plenary Lectures (Weissenberg Awardee Talk)

Tuesday9:00Grand Ball ComplexHow much paint is left on your brush? – A journey in the world of yield stress fluidsPhilippe Coussot

Laboratoire Navier, Université Paris-Est, Champs sur Marne 77420, France

We commonly extract various objects from baths of yield stress fluids (mud, chocolate, cement paste, paint, cream, gel, etc) to coat the material layer remaining on the object over a solid surface (bread, wall, skin, etc). At first sight this operation seems trivial. For simple liquids this is the well-known dip-coating process whose result depends on the competition between viscous, capillary and gravity effects [see e.g. Derjaguin and Levi, 1964)]. But for yield stress fluids the situation is much more complex due to the specific nature of these materials. In particular the volume finally coated can vary from zero to a large value depending on the exact material behavior, the procedure (flow history), and the boundary conditions. Here we explore these different aspects, which gives us the opportunity to review and discuss the state of the art of various problems in the science of yield stress fluids such as: the fundamental rheological behavior of these fluids; the microstructural origin of this behavior; the impact, on flow in complex geometries, of solid-liquid phase coexistence and elasticity in the solid regime; the possibility of shear-banding; the impact and origin of wall-slip; the role and characteristics of thixotropy; and the fate of the material during drying.

Symposium SC

Suspensions and colloids

Organizers: Norbert Willenbacher and Philippe Coussot

Tuesday 10:30 Grand Ball

Structure and dynamics of colloidal short range repulsive interacting suspensions with weak attractive interactions

Clara Weis and Norbert Willenbacher

Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe 76131, Germany

Understanding phase behavior, structure and dynamics of colloidal dispersions is of utmost importance from a scientific as well as from an engineering point of view. In this work, the effect of weak attractive interactions on structure and dynamics of aqueous, polymer dispersions with short range repulsive interactions is investigated using Multiple Particle Tracking (MPT) and classical rotational rheology. This allowed us to correlate microstructure, structural heterogeneities and local particle mobility in fluid, fluid/crystalline, glassy and gel like samples with the corresponding macroscopic flow behavior. For volume fractions below the hard sphere freezing point good agreement between micro- and macro-viscosity was found. As weak attractive interactions were induced by adding non-adsorbing polymer, an enormous broadening of the fluid-crystalline co-existence regime was observed. MPT allowed for retrieving the phase composition, i.e. the fraction of the fluid and crystalline regions as well as the respective particle concentration, completely. In addition, the size of the crystals as well as their shear modulus could be determined. Further increasing attraction strength a gel state occurred and MPT disclosed a heterogeneous structure resembling a percolating network of dense particle clusters in a dilute suspension more than a uniform gel structure. At volume fractions above the glass transition, the introduction of weak attractive interactions leads to a much broader fluid regime than predicted by mode-coupling theory. At a given volume fraction, stronger attractive interaction is required to form an attractive gel than for true hard sphere systems. MPT enables to study particle localization and structural heterogeneities on feasible, short time scales since a large number of dispersed particles are in the field of view.

Tuesday 11:10 Grand Ball

Searching for rheological signatures of jamming transition in soft hairy colloids <u>Léo Gury¹</u>, Dimitris Vlassopoulos¹, Michel Cloître², and Mario Gauthier³

¹Materials science and technology- University of Crete, Foundation for research and technology-Crete, Heraklion, Greece; ²MMC, ESPCI, Paris 75005, France; ³University of Waterloo, Waterloo, Ontario N2L 3G1, Canada

Recently, dense microgel suspensions were shown to exhibit a glass-to-jamming transition characterized by larger yield stress and strain and stronger dependence of plateau modulus on concentration for the jammed state, as well as other fine differences in flow curves. As these microgels have no virtually dangling ends, a natural question is the role of grafted arms of soft colloids (allowing for interpenetration) on this transition. In this work we address this challenge. In particular, we investigate the rheological behavior of highly concentrated solutions of 800-arm star polybutadiene (1,4-addition) in the nearly-athermal solvent squalene. We perform transient shear (step rate)

SC2

experiments and investigate both the build-up of stress and the subsequent relaxation upon flow cessation, as function of both concentration (0 to 100% wt) and shear rate (5x10-4 to 10 s-1). As models among soft colloids, star polymers exhibit a rather well-understood soft interaction potential that depends on the number of arms. Concentrations up to the melt were investigated, hence spanning the gap from solution to melt, while maintaining a low plateau modulus (in the order of 100kPa). Plateau modulus, yield stress and other rheological properties are also investigated against concentration in search for a possible jamming transition inside the glassy regime (C>>C*). The results provide a rather complete experimental test that can serve as basis for understanding the interplay of softness (reflected in interpenetration and shrinkage) and the potential jamming transition throughout a very wide range of concentrations.

Tuesday 11:30 Grand Ball

A closer look at the use of soft thermoresponsive microgels as seemingly ideal model systems for the investigation of the glass and jamming transition

<u>Jérôme J. Crassous</u>¹, Divya Paloli², Maxime Bergman³, and Peter Schurtenberger⁴

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Thermoresponsive particles such as poly(N-isopropylacrylamide) (PNIPAM) microgels, that vary their size as a function of temperature, have been widely used as model systems for soft colloids capable of reaching effective volume fractions Φ_{eff} far above close packing, Φ_{co} , with intriguing structural and dynamic properties [1]. In particular their ability to change size and thus volume fraction with temperature has made them highly attractive model systems for the investigation of liquid solid transitions such as the glass or jamming transition. These generally assume that the interparticle interactions between microgels does not change with temperature, and there seems to be common agreement that this is valid below at temperatures below the collapse or volume phase transition temperature T_{VPT} . Here we now critically re-examine this assumption, and present results from a systematic study of the effect of number density and temperature on the structural and dynamic properties of PNIPAM microgel suspensions. We use a combination of small-angle x-ray and neutron scattering, confocal laser scanning microscopy, mechanical spectroscopy and diffusing wave spectroscopy to investigate microgels at concentrations below and above the glass and jamming transition. We unambiguously demonstrate that the assumption of a temperature-independent interaction potential is not justified even significantly below T_{VPT} , and that the emerging viscoelastic properties of these suspensions are critically influenced by the temperature and their ability to strongly interpenetrate at volume fractions above Φ_{cp} .

Reference

1. P. J. Yunker, K. Chen, M. D. Gratale, M. A. Lohr, T. Still and A. G. Yodh, Rep. Prog. Phys., 2014, 77, 056601-056630.

11:50 Grand Ball Tuesday

Rheological properties of heavy oil and its components as colloidal systems

<u>Alexander Malkin</u>¹, Sergei Ilyin¹, Maria Mironova¹, and Natalya Zadymova² ¹Laboratory of Rheology, Institute of Petrochemical Synthesis RAS, Moscow, Moscow 119991, Russia; ²Chemical Faculty, M.V.Lomonosov Moscow State University, Moscow, Moscow 119991, Russia

This presentation is devoted to the rheology of heavy oils which is one of the main part of the world recourses of hydrocarbons. The central task of the work is searching for the ways to decrease the viscosity of crude heavy oil which is an intriguing task of oil industry. The general basic approach for solving this problem is treating heavy oil as an emulsion containing components of colloidal size. The presentation consists in two parts. First, we have examined the composition of several typical heavy oils and studied the rheology of its components with a view to estimate their role in the high viscosity of heavy oil. Second, we have made experiments devoted to transformation of heavy oil into the direct emulsion in water and examined the role of some surfactants in suppressing the high viscosity of crude heavy oil. Finally, we have examined application of the data of rotational rheometry for designing tube transportation lines and found that this requires caution because one can meet with some special effects due to inhomogeneous character of flow through a tube which look like wall sliding.

Tuesday 12:10 Grand Ball

Shape effects on the rheological behavior of polymer-grafted nanoparticles in solution

Daniele Parisi¹, Dimitris Vlassopoulos², Benoit Loppinet³, Liu Chen-Yang⁴, and Ruan Yingbo⁵

¹Materials science and technology-university of Crete, Foundation for research and technology-Crete, Heraklion, Greece; ²Materials science and technology- University of Crete, Foundation for research and technology-Crete, Heraklion, Greece; ³Foundation for research and technology - Crete, Heraklion, Greece; ⁴Institute of chemistry chinese academy of sciences, Beijing, China; ⁵Instute of chemistry chinese academy of sciences, Beijing, China

The large majority of rheological investigations with soft colloids involve spherical particles. However, in several applications the particles are anisotropic. Here, we focus our attention on polymer-grafted nanoparticles in solution and compare three soft systems with the same chemistry, similar grafting density, same number of monomers per grafted arm but different core shape (spheres, cylinders and lamellas). Solutions in the dense regime at the same mass concentration have been investigated by means of light scattering and rheology in both linear and nonlinear regime. We find that, at the same weight concentration the shape affects substantially the relaxation times, yielding mechanisms and residual stresses, which reflect different particles arrangement in solution. We compare against relevant data in the literature with hard spheres, ellipsoids and other soft spheres, and attempt at extracting a generic phenomenological picture of rheology vs. shape and concentration.

SC4

Symposium NF

Non-Newtonian fluid mechanics and fluid instabilities

Organizers: Natalie Germann and Suzanne Fielding

Amalienborg Helical extrusion instability of strongly shear-thinning polymer solutions Tristan Baumberger¹ and Lise Picaut² ¹Institut des nanosciences de Paris, Paris 75005, France; ²Institut des nanosciences de Paris, Paris 75005, France

Helical instabilities, commonly observed during the extrusion of polymer melts or solutions, are usually ascribed to the detabilization of the flow upstream of the contraction at the inlet of the die. However, probably due to their inherently 3D nature , they remain relatively poorly understood. Using concentrated alginate solutions we have been able to study in details the onset and subsequent growth of the helical disturbance of an extrudate under experimental conditions with almost zero gravity and surface tension. We show that the aspect ratio of the capillary (the die) has no influence on the instability, up to huge values of order 100, whereas the origin of the oscillations can effectively be tracked up to the inlet contraction. We are led to propose that the capillary flow itself is unstable with respect to finite amplitude helical perturbations which can thereby be amplified - rather than damped, as expected for an inlet instability - while being convected downstream. Oscillations with significant amplitudes are only observed in a relatively narrow band of shear rates, indicating that some « resonance » condition is required between the inlet and capillary modes. These features, at odds with the phenomenology previously reported for polymer melts, are possibly ascribable to the strongly shear-thinning rheology of our solutions.

10:50 Amalienborg Tuesday

10:30

Tuesday

Influence of Non-Newtonian effects on the draw resonance instability

Mathias Bechert¹, Dirk W. Schubert¹, and Benoit Scheid²

¹Institute of Polymer Materials, Friedrich-Alexander-Universität Erlangen-Nürnberg, Erlangen, Germany; ²Transfers, Interfaces and Processes, Université Libre de Bruxelles, Brussels, Belgium

The effect of draw resonance limits the applicable parameter space in film casting processes, as it leads to oscillations of velocity and both film thickness and width, if a critical draw ratio, i.e., the ratio of the inlet to the take-up velocity, is exceeded. Non-Newtonian effects like strain hardening and thinning are known to have a large impact on the critical draw ratio.

In this work we analyze a simple film casting model employing several typical viscoelastic constitutive equations by means of linear stability analysis. After an evaluation of an appropriate inlet boundary condition for the stress tensor components, similarities and differences of the various models are discussed and necessary properties of a constitutive equation for a realistic prediction of the critical draw ratio are determined, which is supported by review of available experimental data.

The analysis also provides insight into the mechanism underlying the viscoelastic effect on draw resonance, which is strongly correlated to the process-dependent apparent or effective elongational viscosity. Based on this, the applicability of generalized Newtonian fluid models as an alternative is examined and evaluated.

Tuesday 11:10 Amalienborg

Wall Slip of Polyisobutylenes: Effect of Molecular Characteristics

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Rheology and wall slip behavior of several polyisobutylene (PIB) melts with different molecular weights were determined using parallelplate and capillary rheometry. All PIBs studied were found to slip even at very low shear rates. The transition from weak to strong slip (nearly plug flow) was found to occur at a wall shear stress of approximately 0.078 MPa. A slip model, previously developed by our group, based on double reptation was used in order to relate the slip velocity, V_s, to the molecular weight distribution of the polymers. It was found for the monodisperse polymers (extracted from the general model) that the slip velocity scales with wall shear stress, σ_w , and the number average molecular weight, M_n as $V_s \sim M_n^{-2} \sigma_w^{-1/n}$ with n equal to the local slope of the flow curve of the corresponding polymer. The exponent -2 in the molecular weight dependence for PIBs was found to be the same as previously reported for high-density polyethylenes (HDPEs) and polybutadienes (PBDs), suggesting that it is universal for flexible macromolecules adsorbed on high energy surfaces.

Tuesday 11:30 Amalienborg

Annual European Rheology Conference 2017

Physic origin of the Gross Melt Fracture in SBR melt extrusion

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Extrusion is one of the main processes in the rubber industry for the production of tires treads. However, under certain conditions, various defects and flow instabilities occur, which not only limit the production rates but also influence the appearance and the quality of extrudate products. A melt instability, usually called Gross Melt Fracture is often observed when the extrusion rate is increased beyond a critical value. This instability is characterized by a volume distortion, eventually helical or periodic, rapidly evolving toward a chaotic aspect.

NF2

NF3

NF4

3

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Because Gross Melt Fracture limits the production rate, much attention has been devoted to predict when it will occur. However, there is still no general understanding of the origin of this phenomenon. In this work, we focused on polystyrene-butadiene copolymer (SBR), pure and filled with silica, used in tire applications to understand the physical mechanisms at the origin of this phenomenon. Allal [1] proposed recently a model to determine the critical shear rate at the onset of gross melt fracture, where the critical shear rate is governed by the inverse of the terminal relaxation time and process parameters such as the entrance angle, the capillary length, and the capillary diameter. In this work, we compare the results of this model to the experimental data obtained with different capillary geometries and various SBR compounds. [1] A. Allal, How to postpone the Gross Melt Fracture in linear polymer melt extrusion, Annual Conference of the Polymer Processing Society, Lyon (France), 2016.

Tuesday 11:50 Amalienborg

Extrusion melt flow instabilities in long chain branched polyethylenes

Roland Kádár

Department of materials and manufacturing technology, Chalmers University of Technology, Gothenburg, Sweden

The influence of molecular weight and long chain branching of low density polyethylenes (LDPE) on the onset and development of extrusion instabilities was investigated in this study. Four commercial LDPEs (LyondellBasell; P1-4) were compared. The samples allow for the cross-comparison of increasing long chain branching (LCB) at low and high M_{-w} . The extrusion flow experiments were performed on a Brabender 19/25D single screw extruder equipped with a compression screw (2:1) and a slit die (20×2×100 mm; die temp.: 140C). A die apparent shear rate ramp rate of 0.039 s⁻² was imposed to insure the same flow history. In-situ mechanical pressure fluctuations were acquired using a conventional melt pressure transducer (Terwin 2000) and the oversampling technique. Inline extrudate optical video recordings were performed at 60 and 200 fps, with spatio-temporal diagrams therefrom created. The in-situ pressure fluctuations and the grey image intensities were then analyzed via Fourier-transformation and compared. The rheological characterization of the polymers was performed on an Anton Paar MRC702 TwinDrive. The presence of instabilities was detected for all samples using the two analysis methods and consisted of low frequency surface distortions. Both increasing M_{-w} and LCB. For high M_w (P3 and P4) a decrease in LCB resulted in Wi₁ = 6 (P3) whereas for low Mw (P1 and P2) the decrease in LCB resulted in Wi₁ = 13 for P2 and Wi₁ = 29 for P1. The samples with high M_{-w} and LCB (P1) had a stabilizing effect on the flow with Wi₁ = 29. Furthermore, a supercritical transition was recorded for P1 (Wi₂ = 174) resulting in an extrudate pattern having two characteristics frequencies.

Tuesday 12:10 Amalienborg KNUCKLE FORMATION FROM MELT ELASTICITY IN PLASTIC PIPE EXTRUSION

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When plastic pipe is solidified, it proceeds through a long cooling chamber. Inside the chamber, inside the extrudate, the plastic is molten, and this inner surface solidifies last. Sag then happens inside this cooling chamber, and sometimes, thickened regions (called knuckles) arise in the lower quadrants of the pipe, and specifically in large diameter thick-walled pipes. To compensate for sag, we normally shift the die centerpiece downward. Here, we investigate this die eccentricity, and its remarkable interaction with fluid elasticity in knuckle formation in annular flow of polymeric liquids. We develop a map to help plastics engineers predict the extrudate shape, including extrudate knuckles, and then from the mass balance over the postdie region, to predict the extrudate shape entering the cooling chamber. We find that Newtonian extrudates, or extrudates for small pipe, never knuckle. Both of these findings agree with industrial experience. We also include a worked example to help plastics engineers suppress extrudate knuckling.

Symposium SM

Polymer solutions and melts

Organizers: Giovanni Ianniruberto and Qian Huang

Tuesday 10:30 Christiansborg

SM1

i-Rheo GT: Transforming G(t) obtained from molecular dynamics simulations into the materials' linear viscoelastic properties without artefacts

Manlio Tassieri

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I present a new analytical tool for educing the materials' linear viscoelastic (LVE) properties from (atomistic and quasi-atomistic) molecular dynamics simulations (MDS) describing the temporal behaviour of the materials' shear relaxation modulus G(t). The new tool allows the evaluation of the materials' complex shear modulus $G^*(\omega)$ over the widest range of experimentally accessible frequencies, without the adoption of 'preconceived' models, such as a generalised Maxwell model. This is achieved by means of the analytical method introduced by Tassieri *et al.* [1,2] to evaluate the Fourier transform of raw data, via: $G^*(\omega)=i\omega\Ĝ(\omega)$ where $\Ĝ(\omega)$ is the Fourier transform of G(t) and ω is the angular frequency. The analytical method has been implemented into a new open access executable named 'i-Rheo GT', enabling its use to a broad scientific community. The effectiveness of the new rheological tool has been corroborated both by analysing the dynamic response of a model system (i.e., a single Maxwell mode) and by direct comparison with bulk-rheology experimental data. i-Rheo GT offers the opportunity to gain new insights into the materials' LVE properties, especially at high-frequencies (i.e., in the glassy region

NF6

NF5

SM₂

and beyond); where (i) conventional tools (e.g., Reptate or Iris) struggle to 'interpret' the data and (ii) MDS actually provide the most accurate predictions of G(t). Interestingly, these frequency regions are commonly 'unexplored' by the rheology community. Nevertheless, having access to atomistic and quasi-atomistic MDS represents both a challenge and a springboard for theoreticians to develop comprehensive models able to predict the materials' LVE properties over the widest range of experimentally accessible frequencies; hence, the importance of the new rheological tool.

Tuesday 10:50 Christiansborg

Investigation of drug-loaded polycaprolactone strands for 3D printing of personalized medicine

Magnus Edinger, Johanna Aho, Natalja Genina, Johan P. Bøtker, and Jukka Rantanen

Department of Pharmacy, University of Copenhagen, Copenhagen 2100, Denmark

This study focused on identifying the critical rheological and solid-state properties of polymer-drug combinations used for 3D printing of medicinal products using fused-deposition modeling (FDM). In a typical FDM process, a drug-containing solid strand is fed into the nozzle of the 3D printer where it melts and is deposited layer-by-layer, finally forming the desired 3D geometry. During feeding into the nozzle, the strand should be flexible, but remain hard enough prior to melting in order to act like a piston that facilitates continuous movement of the melt through the nozzle. A number of critical parameters affect the printability of these strands. Suitable stiffness and ductility are critical for the feeding of the strand into the nozzle and the melt must flow steadily, depositing a layer with minimal thickness variation upon being extruded from the nozzle. Finally, the thermal properties and solubility of a given drug into the polymer influence the solidification of the deposited melt. Dynamic mechanical analysis (DMA), differential scanning calorimetry (DSC) and rheometry were used to investigate the tensile modulus and the complex viscosity of 4 different mixtures of the model drug indomethacin (IND) and the model polymer polycaprolactone (PCL) in the ratios IND:PCL, 10:90, 30:70, 50:50, 70:30 (n=3). Pure PCL and IND:PCL 10:90 had the same tensile modulus, while it increased for all other samples due to the increasing amounts of undissolved solid IND being dispersed in the PCL matrix. The viscosity decreased for 10:90 and 30:70 compared to pure PCL due to IND acting as a plasticizer, and increased for 50:50 and 70:30 due to solid IND being dispersed in PCL. The increased content of solid IND in the PCL matrix was confirmed by DSC results. All strands except 70:30 were printable using a MakerBot 3D printer at 100 degrees celsius. The use of DMA and rheometry allows assessing the 3D printability of drug-polymer mixtures.

Tuesday 11:10 Christiansborg

SM3

New approach for modeling polymer modified bitumens as polymer solutions: power-law scaling of rheological constants

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Bitumen is often modified with polymers to enhance its properties in various engineering applications such as asphalt technology. Nevertheless, there is no clear quantitative understanding of how the rheological properties of polymer modified bitumens (PMB) evolve as a function of polymer concentration. This study develops a framework for predicting rheological properties of PMBs based on those of the pure components. For this investigation, bitumen samples modified with different amounts ($\Phi \approx 0.03-0.11$) of styrene-butadiene-styrene (SBS) triblock copolymer are prepared. Fluorescence microscopy reveals that SBS swells up to nine times its initial volume in bitumen and forms a continuous elastic network already at relatively low polymer concentrations. Analysis of the small-amplitude oscillatory shear (SAOS) properties of the SBS modified bitumens as well as of the pure components demonstrates that SBS modified bitumens can be considered as semidilute entangled polymer solutions in which bitumen act as a Newtonian solvent. The plateau modulus and steady-state recoverable compliance are observed to exhibit power-law concentration dependences $G_N^0 \sim c^a$ and $J_e^0 \sim c^{-a}$ where $a \approx 2.3$. These results are in excellent agreement with theoretical predictions for associative polymer solutions. It is also demonstrated that the concentration-dependent G_N^0 and $J_e^0 \sim c^{-4.2}$ as homopolymer solutions. The power-law concentration dependence of the zero-shear first normal stress coefficient $\psi_{1,0}$ is also examined.

Tuesday 11:30 Christiansborg

SM4

understadning the Molecular processes leading to necking in extensional flow of polymer solutions: using microfluidics and single DNA visualization

Pouyan Boukany

Delft University of Technology, delft, The Netherlands

In this work, we investigate the necking and pinch-off dynamics of polymeric liquids by combining micro-fluidics and single DNA observation. Polymeric droplets were deformed and stretched by passing them through the stagnation point of a T-shaped micro-fluidic junction. In contrast with the sudden breakup of Newtonian droplets, a stable neck is formed between the separating ends of the droplet which delays the breakup process. Initially, polymeric fi laments. These filametns are exposed to the exponential thinning with extensional flow within them. Later, thin polymeric fi laments develop a well-known beads-on-a-string morphology along their length and finally rupture during the final stages of the thinning process. To understand the molecular picture behind these phenomena, a T-shaped microfluidic device was integrated with advanced fluorescence microscopy to visualize stained polymer molecules at the stagnation point in the necking region. We found that the individual polymer molecules suddenly stretched and elongated from their coiled conformation at the onset of necking. The extensional flow inside the neck was strong enough to stretch polymer chains, however, they display a broad

distribution of the molecular extensions due to molecular individualism. In addition, we study the dynamics of single molecules during formation of beads-on-a-string structure. We observe that polymer chains gradually recoil inside beads while polymer chains between beads remain stretched to keep the connection between beads.

11:50 Christiansborg Tuesday

Rheology of fiber spinning from polymer solutions

Valery G. Kulichikhin¹, Alexander V. Semakov², and Ivan Y. Skvortsov³

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The opinion exists that the main kind of deformation at fiber spinning is the uniaxial extension. However, the role of shear flow in spinneret channels is also very important. By other words, the combined influence of shear and extension leads to the complex stressed state of solution jets on the first stages of spinning. This situation is considered on an example of PAN solutions in dimethylsulfoxide, and PAN and cellulose solutions in N-methylmorpholine-N-oxide. The main attention was directed to extremely high shear and extension stresses causing the phase separation effect. It was shown that it is possible to reach separation of solution on polymer and solvent phases (unstable state) by summarizing of both kinds of strain. The responsible for the phase separation is accumulated in strong flows elastic forces. The observed phenomenon gave food for new constitutive rheological model partially explaining input of the regular instability as for neat polymer solutions, as for filled with nanoparticles. From application viewpoint phase separation of polymer solutions at high shear or extension rates allowed us to realize fiber spinning without coagulation bath (so-called mechanotropic spinning).

12:10 Christiansborg Tuesday

SM6

Characterization of Dilution Effect of Semi-dilute Polymer Solution on Intrinsic Nonlinearity Q0 via FTrheology

Hyeong Yong Song¹, Seung Joon Park², and Kyu Hyun¹

School of Chemical and Biomolecular Engineering, Pusan National University, Busan, Republic of Korea; ²Department of Chemical Engineering and Biotechnology, Korea Polytechnic University, Siheung-si, Republic of Korea

Intrinsic nonlinearity Q0 under medium amplitude oscillatory shear (MAOS) deformation was investigated for monodisperse polystyrene (PS) solutions with various concentrations, which were classified into unentangled and entangled solutions in semi-dilute condition. Two groups of PS solutions displayed different shapes of Q0 as a function of frequency. Unentangled solutions showed increases of Q0 with frequency at low frequency region and then the plateau behavior at high frequency region. On the contrary, entangled solutions showed increase of Q0 before the maximum (Q0,max) and then decrease after it, which is similar to the behavior of entangled linear polymer melts. Q0 curves of each group were superposed in a dimensionless coordinate (Q0/Q0,max vs. De), so that transition from the plateau of Q0 to decrease of Q0 might indicate onset of entanglements in polymer solutions. In particular, Q0, max of all unentangled solutions indicated the same value of 0.006 regardless of polymer concentration, because Q0 responds to Rouse-like relaxation process only, which is featured as no interchain interaction and chain stretching. However, Q0,max for entangled solutions was dependent on the number of entanglements (Z). A master curve of Q0,max as a function of Z showed Q0,max is constant at low entanglement number (few or virtually no entanglements), and then increases at the beginning of entanglements and approaches a limiting value at higher entanglement number, where reptation is a dominant relaxation process. Furthermore, master curve of Q0,max as a function of Z was used to quantify degree of tube dilation based on the dynamic tube dilution (DTD) theory. Direct comparison of Q0,max between semi-dilute solutions and melts showed they follow the same molecular dynamics in MAOS deformation like SAOS. Comparison between static and dynamic dilutions using the master curve of Q0,max suggested this master curve could characterize the effective number of entanglements per backbone chain in branched polymers.

Symposium FB

Food and biorheology

Organizers: Henrik Kragh and Ulf Andersen

Tuesday 10:30 Fredensborg How good are Humans at differentiating rheological Behavior? Jan Engmann and Adam Burbidge Nestlé Research Center, Lausanne 1000, Switzerland

Rheological science has developed concise descriptions for the constitutive behavior of complex liquids and soft solids across a wide range of length and time scales. For the performance of many consumer products, the differences in rheological behavior perceived by humans can be decisive, which poses recurrent questions about the best performing objective and subjective methods for screening and selection of prototypes. Our paper will illustrate by a few classical and recent examples our current understanding how humans discriminate rheological features and give a fresh perspective for an efficient constitutive approach using concepts of fractional calculus, based on pioneering work by Scott Blair in the 1940s.

SM5

Tuesday 10:50 Fredensborg

How the type of exopolysaccharide affects the rheological properties of fermented products

Georg Surber, Susann Mende, Victor Constantinescu, Doris Jaros, and Harald Rohm

Chair of Food Engineering, Technical University of Dresden, Dresden, Germany

Exopolysaccharid (EPS)-producing lactic acid bacteria (LAB) are widely used in the manufacture of fermented dairy products (yoghurt, cheese) to improve texture without adding hydrocolloids. EPS from LAB can be distinguished either by their location into free EPS present in the medium (fEPS) and capsular EPS attached to the bacterial cells (cEPS), or by the effects they evoke into ropy and non-ropy EPS. Although texture-enhancing effects of in situ produced EPS are generally acknowledged, little is known on the specific impact of a particular type of EPS.

To gain more information on this issue we used two Streptococcus thermophilus strains (one producing non-ropy, capsular EPS, the other ropy, free EPS), and investigated the rheological properties of both the fermentation medium used for starter culture manufacture and the final fermented dairy products. Fresh cheese was produced in laboratory scale from milk with 14 g/100 g dry matter and, after fermentation, processed further by heating, shearing and centrifugation. Milk gels and fresh cheese were characterised by rheological and physical methods (e.g. hysteresis loop, flow curve, syneresis) and an analytical optical centrifuge (e.g. phase separation).

Depending on the type of EPS, the two S. thermophilus strains caused different rheological behaviour. Medium with fEPS showed a higher viscosity than the medium with cEPS, and shearing decreased viscosity of the fEPS medium significantly. Preliminary results of fresh cheese also indicate a different behaviour during processing and in the final product. For fresh cheese produced with a cEPS strain a larger hysteresis loop area was observed (~ 37 kPa/s) compared to fEPS strains (~ 29 kPa/s), which indicates a higher shear stability for fEPS producing strains. Further experiments concerning the characterisation of fresh cheese with other rheological methods and an analytical photo centrifuge are under progress.

Tuesday 11:10 Fredensborg

An investigation of the effect of molecular interactions on the rheological properties of LMW organogels in edible oils

Francesca R. Lupi¹, Valeria Greco¹, Noemi Baldino¹, Bruno de Cindio¹, Peter Fischer², and Domenico Gabriele¹ ¹DIMES, University of Calabria, Rende, Cs 87036, Italy; ²Institute of Food, Nutrition and Health, ETH Zurich, Zurich 8092, Switzerland

A deep investigation of the rheological properties of edible organogels was coupled with their microstructural characterisation based on different techniques (calorimetry, nuclear magnetic resonance, infrared spectroscopy, rheology, polarised light microscopy). The main aim of the work was the better understanding and control of the oil gelation phenomena in Low Molecular Weight organogels based on vegetable oils. In this study MAGs (monoglycerides of fatty acids) and policosanol were used as gelators. Dynamic moduli were related, via a fractal model, to microstructural characteristics such as solid fat content and fractal dimension. Infrared spectroscopy evidenced that hydrogen bonding was the leading force necessary for building network structure in MAGs gel, whereas in policosanol system the intermolecular interactions are mainly van der Waals forces. Because of the different relative contribution of molecular interactions, the investigated organogelators exhibit a distinguished macroscopic behaviour; MAGs are sensitive to the nature of oil (solvent) and structuration occurs quickly, even though at a temperature lower than policosanol. On the contrary, policosanol organogels exhibit a behaviour independent of the used oil and a slower gelation rate. Nevertheless, at lower concentration a stronger final gel, due to the large number of interactions arising among the long alkyl chains of the fatty alcohols is obtained.

Tuesday 11:30 Fredensborg

FB4

Rheological properties of gluten-free bread systems, based on resistant starch and vegetable proteins treated with transglutaminase

Noemi Baldino¹, Francesca Laitano², Francesca R. Lupi³, and Domenico Gabriele⁴

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Gluten plays a relevant role in maintaining the appearance and structure of baked gods. If removed, this can prevent the dough from properly developing during the kneading, baking and leavening stages. Gluten-free (GF) alternatives flours, when mixed with water, are unable to generate dough with suitable viscoelastic properties, leading to final baked products which lack in appropriate texture and appearance. GF products are mainly based on starch of different botanical sources, bringing a limited amount of proteins and fibers in the diet. Resistant starch represents an alternative to the most commonly used starches. It is classified as a dietary fiber because it is not digested in the small intestine and it can also help in preventing some serious diseases. Proteins from different botanical sources such as pea, soy and hemp, are also widely used in the enrichment of GF bread formulations with the role of nutrients and as structure and texture forming agents. An improvement in dough texture and appearence in bread making has been reported also when using enzymes. A possible way to improve the structure of GF breads could be the employment of transglutaminase (TGase) that catalyzes proteins' cross-linking. In the current work a study of GF bread formulations, based on resistant starch, proteins and using TGase, has been carried out, in order to obtain a GF bread enriched in fibers with improved texture. The impact on its final structure of three proteins employed at different levels and treated with TGase was evaluated with the aim of obtaining a formulation with texture as closer as possible to wheat-based dough. The study involved an investigation of mechanical properties of the mixtures performing oscillatory measurements and compression tests.

FB3

Tuesday 11:50 Fredensborg Oleofoams : properties of crystal coated bubbles from whipped oleogels - evidence for Pickering stabilization

<u>Deniz Z. Gunes</u>¹, Mathieu Murith², Julie Godefroid³, Cindy Pelloux⁴, Hélène Deyber⁵, Olivier Breton⁶, and Olivier Schafer⁷ ¹Nestlé Research Center, Lausanne, Switzerland; ²Nestlé Research Center, Lausanne, Switzerland; ³Nestlé Research Center, Lausanne, Switzerland; ⁴Nestlé Research Center, Lausanne, Switzerland; ⁵Nestlé Research Center, Lausanne, Switzerland; ⁶Nestlé Research Center, Lausanne, Switzerland; ⁷Nestlé Research Center, Lausanne, Switzerland;

Interfacially stabilized non-aqueous lipid based foams, which we name here "oleofoams", are rarely encountered as opposed to the high number of emulsifiers, synthetic or natural, stabilizing aqueous foams. Such systems offer high potential for new textures with nutritional benefits such as reduction of fat or of saturated fatty acids (SFA). For the few non-aqueous food foams that are believed to be stabilized by interfacial effects, insufficient evidence is present for supporting and assessing the interfacial contribution to stability. We bring here complete evidence that lipidic crystals made of a high fraction of fully soluble monoglyceride (MG) in oil, do not only adsorb at the oil-air interface, but can easily form a jammed closely packed layer of crystals around the bubbles of a foam produced by whipping (Pickering effect). A thin, jammed layer of crystals on bubbles can cause bubbles to retain non-spherical shapes in the absence of bulk effects for times much longer than the characteristic relaxation time of capillary relaxation for bare bubbles, which is actual evidence for interfacial stabilization of Pickering type. The stability of foams (up to 75% air content) obtained from prolonged whipping was compared to that of foams created by depressurization following gas dissolution in the gel, showing that whipping is necessary for bubble wrapping with a layer of crystals. The origin of high stability against Ostwald ripening at long times is also discussed. Furthermore, we could show that these Pickering "whipped foams" have rheological properties dominated by interfacial or film contributions, which is of high interest for food and cosmetic applications due to their high moduli. This system can be considered a model as the crystallization behavior of the MG used is similar to many fats. Last but not least, our methods are very general in the context of lipid based foaming, in particular from food materials, and were used in patent applications.

Symposium SG

Solids, glasses, and composites

Organizers: Jeppe C. Dyre and Esmaeil Narimissa

Tuesday 10:30 Kronborg

A combined method for electrical conductivity measurement of polymer composites under extensional deformation

Marjorie Marcourt, René Fulchiron, and Philippe Cassagnau

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The addition of Carbon Nanotubes (CNT) to polymer has paved the way to ultra-low filled nanocomposites characterized with both electrical and mechanical properties. In the last decades, those materials have been a great topic of studies, particularly as concerns the rheological behavior and electrical characteristics under shear rate. Those works have, amongst others, highlighted the drastic structural change of the filler network under external forces. To go further in the comprehension of the filler network deformation/destruction during melt deformation, this work focuses on the deformation of the CNT network in elongated polymer melts by a combination of conductivity monitoring and extensional rheological measurement. For this specific purpose, an Extensional Viscosity Fixture (EVF) accessory of a rotational rheometer ARES has been modified to allow the sample conductivity measurement during extensional test. As the polymer matrix is electrically insulating, the measured current is characteristic of the percolated CNT network.

This new set-up gives access to the electrical conductivities variation of the material under extensional forces and makes possible the determination of the maximal Hencky uniaxial deformation that nanocomposites can undergo before becoming electrically insulating. Indeed, first results have shown that the conductivity of CNT/polymer nanocomposites can present a sharp decrease before the sample break. Moreover, a strong sensitivity to both temperature and extensional rate has emerged revealing the prevailing role played by the molecular dynamics. The results have been correlated to experimental conditions via the introduction of the Weissenberg number.

Keywords : Extensional rheology, Nanocomposites, Weissenberg number, Carbon Nanotube.

Tuesday 10:50 Kronborg

Multi-scale modelling methodology for biobased polymer fibre composites

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For fully biobased polymer fibre composites a multi-scale modelling methodology is implemented to connect manufacturing conditions with material parameters, polymer dynamics and product properties. The scheme aims to design macroscale processing conditions for the fibre spinning and composite fabrication process, meso-scale morphology as well as micro- scale molecular structure to achieve ultimately desired mechanical properties. (1) The molecular dynamics modelling results relate to the properties of the pure polymer phases and are linked to the phase-field and continuum modelling via characteristic material parameters or functions. For example, the molecular mobility and time-scale dependence on molar-mass distribution and temperature will be taken into account for the phase-field models of polymer

SG1

SG2

SG3

crystal morphology evolution. The mechanical properties of two-phase composite materials consisting of reinforcement fibres embedded in a polymer matrix are typically calculated by continuum micromechanical models. The models are written up for representative volume elements in the materials and this includes geometrical parameters for the composition (e.g. fibre content and orientation) and material parameters (e.g. crystal structure, strength, stiffness of both phases). Such micromechanical models have been validated for short fibre composites manufactured by injection moulding and compression moulding. For fabric based composites, classical laminate theory is used for materials relations together with the determined elastic constants of single plies.

(1) D. Auhl, B. Madsen: 2nd International Workshop on Software Solutions for Integrated Computational Materials Engineering, Barcelona, April 2016

"The research leading to these results has received funding by the H2020 Framework program of the European Union under grant agreement N° 685614"

Tuesday 11:10 Kronborg

Smart magneto-responsive carbonyl iron/natural rubber composites and their viscoelasticity <u>Hyoung Jin Choi</u>¹, Seung Hyuk Kwon², and Tae Hong Min³

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Magnetorheological (MR) elastomers are solid analog of MR fluids whose viscoelastic properties can be finely altered by a magnetic field strength applied. MR elastomers consist of magnetic particles such as carbonyl iron (CI) and iron oxide in an elastomer matrix such as natural rubber and silicone rubber. In this study, we examined effect of CI particle grade and particle orientation on their MR properties. To confirm the orientation of the magnetic particles of the CI/ natural rubber elastomer composite, a mapping method through scanning electron microscope was used. Rheological properties of the MR elastomers under magnetic field were investigated by a rotational rheometer equipped with a magnetic field supplier. Dynamic moduli of the MR elastomer samples, indicating the viscoelastic properties of the samples, were obtained from both strain amplitude and frequency sweep tests. The results showed that as the magnetic field strength increases, the storage moduli increased depending on the angular frequency at a constant shear strain. Higher MR performance from both the viscoelastic characteristics and MR efficiency were also observed for the anisotropic MR elastomer compared to the isotropic MR elastomer. Their MR efficiency and damping factor were also investigated.

Tuesday 11:50 Kronborg

The influence of rheological changes during sonication of poly(ethylene oxide) solutions containing magnetic nanoparticles on morphology of nanofibrous mats

Petr Filip and Petra Peer

Institute of Hydrodynamics, Acad. Sci. Czech Rep., Prague, Czech Republic

Morphology of nanofibrous mats formed by poly(ethylene oxide) (PEO) with distributed magnetic nanoparticles (about 20 nm in diameter) was evaluated in dependence on time of sonication of the initial polymer solutions (PEO dissolved in distilled water). The solutions were exposed to sonication (intensity 200 W, frequency 24 kHz) for 10, 30, and 60 minutes. In contrast to electric conductivity and surface tension, rheological characteristics (viscosity, storage and loss moduli) strongly depend on time of sonication (particularly phase angle). The rheological measurements were carried out also in presence of external magnetic field with the aim to analyse homogeneous distribution of magnetic nanoparticles in polymer solution. Magnetorheological efficiency (a relation of corresponding viscosities) was determined for 80, 170, and 255 mT. Consequently, it was shown that changed rheological characteristics participate significantly in the process of electrospinning and resulting quality of the obtained nanofibrous mats. Acknowledgement: The authors wish to acknowledge the Grant Agency CR for the financial support of Grant Project No. 17-26808S.

Tuesday 12:10 Kronborg Influence of modified nano silica particles on compatibility of linear low-density polyethylene/poly (lactic acid) blends

Ali Haghtalab¹ and <u>Maryam Hoseini²</u>

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In this work the use of modified silica (SiO2) nanoparticles as compatibility agent in immiscible linear low-density polyethylene/ poly (lactic acid) (LLDPE/PLA) blends have been studied. To improve the hydrophobicity properties of the nano particle silica its surface was treated by hexadecyltrimethoxy silane agents. The composites blends were prepared by batch mixing method. The effects of modified silica nano particles, and PLA content on morphology and rheological properties of the samples have been examined. Rheometry measurement and scanning electron microscope (SEM) images were used for investigation of the rheological and morphological behaviors of the nano composites blends. The results of rheological measurements are shown that incorporation of modified silica nano particles into LLDPE/PLA blend enhances the complex viscosity and storage modulus in comparison to LLDPE/PLA without silica. The good morphology in the LLDPE/PLA/modified silica blends presented that modified silica nano particles have improved the compatibility between the PLA and LLDPE phases. As results showed the modified silica nano particles acted as compatibility agent for the LLDPE/PLA blends used in this study.

SG5

SG4

Symposium GS

Gels and self-assembled systems

Organizers: Moshe Gottlieb and Henning H. Winter

Tuesday 10:30 Schackenborg

The viscosity of aliphatic isocyanurates

<u>Dirk Jacques Dijkstra¹</u>, Piet Driest¹, Luís Silvino Alves Marques², Marta Maria Duarte Ramos², Veniero Lenzi², Dirk W. Grijpma³, Dimitrios Stamatialis³, and Frank U. Richter¹

¹CAS-R&D, Covestro Germany AG, Leverkusen, Germany; ²Center of physics, University of Minho, Minho, Portugal; ³Biomaterials science and technology, University of Twente, Enschede, The Netherlands

The production, processing, and application of aliphatic isocyanate (NCO)-based thermosets such as polyurethane coatings and adhesives are generally limited by the surprisingly high viscosity of tri-functionality and higher functionality isocyanurates. These compounds are essential crosslinking additives for network formation. However, the mechanism by which these high viscosities are caused is not yet understood. Model aliphatic isocyanurates were synthesized and isolated in high purity, and their viscosities were determined. It was shown that the presence of the NCO group has a strong influence on the viscosity of the system. From density functional theory calculations, a novel and significant bimolecular bond was identified between NCO groups and isocyanurate rings, confirming the important role of the NCO group. This NCO-to-ring interaction was proposed to be the root cause for the high viscosities observed for NCO-functional isocyanurate systems. Molecular dynamics simulations carried out to further confirm this influence also suggest that the NCO-to-ring interaction causes a significant additional contribution to viscosity.

Tuesday 10:50 Schackenborg

GS2

GS1

Sol-gel transition and phase diagram of ionic-liquid polymer hydrogels (PILs) investigated by rheological measurements

Olivier Ratel¹, Jean-Charles Majesté², Cyrille Monnereau³, and Christian Carrot⁴

¹CNRS, IMP UMR 5223, Univ Lyon, UJM-Saint-Etienne, SAINT-ETIENNE, France; ²CNRS, IMP UMR 5223, Univ Lyon, UJM-Saint-Etienne, SAINT-ETIENNE, France; ³CNRS, Laboratoire de Chimie, UMR 5182, Univ Lyon, ENS-Lyon, LYON, France; ⁴IMP, CNRS UMR 5223, Univ Lyon, UJM-Saint-Etienne, SAINT-ETIENNE, France

Most sustainable energy sources rely on the production of electrical energy. In the last decade, lithium ion based batteries have emerged as interesting candidates as high-density energy storage devices, enabling the developments of electrical vehicles of constantly growing autonomies. The synthesis of polymer electrolytes and the study of their electrochemical properties is currently a very active topic. Poly(ionic liquids) (PILs), in particular, constitute an increasingly sought-after category of materials, as they are expected to replace flammable, leakage-prone organic solvent electrolytes in future energy storage devices.

In this work, we have developed two new polymers (PILs) for energy storage application with two kinds of end groups: phosphonic (PO_3H) or ethyl and an imidazolium group on the polymer backbone with a bromide counter ion. We focus this study on the influence of the cross linking amount on the gel formation mechanism. Hydrogels formed from PILs and water show usual yield stress fluid properties and sol-gel transition is controlled by polymer concentration, cross linking amount and nature of end group. Gelation was studied by means of rheology in small strain oscillatory mode and in strain-rate frequency superposition (SRFS) to build a phase diagram with gel and liquid domain.

From molecular modelisation, a gel structure has been proposed and has been confronted with rheological measurements. Gel formation mechanism appears to be controled by supramolecular bond or friction depending on the concentration and end group.PO₃H end group enables creation of a supramolecular network and thus fast recovery after deformation.

Tuesday 11:10 Schackenborg

GS3

Using Creep testing as an alternative to Multiwave Oscillation for determining the true gel point of network polymers

Mats Larsson¹, John Duffy², Shona Murphy³, and Adrian Hill⁴

¹Malvern Instruments Nordic AB, Uppsala 75228, Sweden; ²Malvern Instruments Ltd, Malvern WR141XZ, United Kingdom; ³Malvern Instruments Ltd, Malvern WR14 1XZ, United Kingdom; ⁴Malvern Instruments Ltd, Malvern WR14 1XZ, United Kingdom

A common method for monitoring gelation dynamics with a rheometer is to perform Small Amplitude Oscillatory Shear (SAOS) testing at a single frequency while monitoring the evolution of G' and G" with time or temperature - the point of gelation being defined as the time or temperature at which the moduli cross. It has been shown that for most systems the true gel point does not coincide with the intersection of the dynamic moduli and is more accurately identified as the time or temperature at which G' and G" become parallel and the loss tangent (tan d) frequency independent. To accurately determine the gel point using SAOS requires measurements at multiple frequencies and at various stages of the gelation process. A common approach is to perform Multiwave Oscillation where frequency dependent moduli are determined simultaneously at several discrete frequencies by applying a complex waveform consisting of a fundamental frequency and several harmonics. This approach can significantly reduce the time required to obtain a frequency spectrum and hence assist in the determination of the true gel point but it is still limited by the time required for a full or partial oscillation at the lowest frequency. Hence, the approach is only really valid for relatively slow curing systems. Furthermore, the sum of the stress or strains applied at each frequency must be within the LVR thereby increasing the harmonic distortion compared with a single frequency test. We propose an alternative to

GS4

GS5

multiwave that overcomes many of these limitations. The approach is based on creep testing and the subsequent transformation of creep compliance to viscoelastic moduli. Furthermore, a frequency spectrum can be acquired in a fraction of the time required for multiwave without the same stress or strain limitations, allowing more weakly structured and faster gelling systems to be evaluated. We will show that it is possible to determine the true gel point for a number of network polymer systems using this approach.

Tuesday 11:30 Schackenborg

Study about the foaming cell development for the epoxy resin containing various curing and blowing agent concentrations

Seung Hak Lee and Kyu Hyun

School of Chemical and Biomolecular Engineering, Pusan National University, Busan, Republic of Korea

The effects of curing and blowing agent concentration for the epoxy resin were studied by rheological, mechanical and morphological approach. The curing time was determined using a differential complex modulus (G*) from the time sweep test. The curing time decreased with increasing amount of curing agent at the fixed blowing agent concentration. On the other hand, by increasing blowing agent at the fixed curing agent concentration, the curing time presented a local minimum value. Minimization of the curing time is quite useful for reducing the processing time. Axial normal forces as a function of time showed a relationship between the contraction force by the curing process and the expansion force by foaming process. From the axial normal force measurement, it could be categorized quantitatively into three parts: the curing dominant region (negative axial normal force development), transition region, and the foaming dominant region (positive axial normal force development). At the transition region, the axial normal force development was delayed because the foaming process was disturbed by the contraction. Mechanical and structural analysis were conducted for the fully cured and foamed epoxy resin. The completely developed epoxy foams with the high curing agent concentration become brittle. On the other hand, they contained well-distributed unit cell foams inside. This is because the fast curing process interrupts the coalescence of the closed foams. Overall, the optimal curing and blowing agent concentration for the epoxy resin could be determined from rheological analysis during the process and mechanical and structural analysis for fully cured and foamed epoxy resin.

Tuesday 11:50 Schackenborg

Solution and gel-properties of ultra-high molecular weight polyethylene in good and poor solvents

André Brem, Raphael Schaller, Jan Vermant, and Theo Tervoort

Soft Materials, ETH Zürich, Zürich, Switzerland

Recently the gel-spinning of high-performance polyethylene (HPPE) fiber precursor from "green" solvents, such as vegetable oils, was demonstrated. In comparison to the use of precursor fibers crystallized from traditional solvents such as decalin, for a given polymer concentration, even better properties could be achieved by using precursor fibers crystallized from solvents with a remarkably poorer solvent quality.

The reasons for the improved performance were not evident and the results are questioning the established concept of the reduced entanglement density in solution being solely responsible for drawability. In this study, a systematic approach, aiming at the identification of factors affecting drawability in the gel-spinning process as a function of solvent quality, is presented. The study is divided into four parts, corresponding to four main stages of the gel-spinning process: rheological properties of the polymer solution, the gelation process, mechanical properties of the resulting gel and drawing behavior of the polymer fiber precursor. Throughout the study, measurements were performed for different polymer concentrations in good and poor solvents.

First, the linear viscoelastic behavior of polymer solutions is investigated, with a focus on differences in the molecular weight between entanglements and the zero-shear viscosity of solutions of good and poor solvents (at equal volume fraction). Second, the gelation process is analyzed using the Winter-Chambon method for near critical gels, addressing gelation time, gel strength and relaxation exponent in dependence of undercooling. The final gel and fiber precursor are characterized by the means of isothermal dynamic mechanical analysis in shear and compression, as well as simple uniaxial compression. Finally, the correlation of the observed properties of the gel, with the drawability of the polymer fiber precursor, will be discussed.

Tuesday 12:10 Schackenborg

Rheology of dopamine containing polymers

Florian J. Stadler¹, Saud Hashmi², Ghavaminejad Amin³, Mohammad Vatankhah-Varnoosfaderani⁴, and Chandra S. Biswas¹ ¹College of Materials Science and Engineering, Shenzhen University, Shenzhen, Guangdong 518060, China; ²Department of Chemical Engineering, NED University of Engineering & Technology, Karachi, Pakistan; ³D epartment of Bionanosystem Engineering, Chonbuk National University, Jeonju, Republic of Korea; ⁴Department of Chemistry, University of North Carolina at Chapel Hill, Chapel Hill, NC 27599-3290, United States

Stimuli-responsive polymer solutions consisting of 95 mol% N-isopropylacrylamide and 5mol% dopamine methacrylate (NIDO5%) were synthesized as precursors for stimuli-responsive gels. To produce gels, the polymer was dissolved in either water or organic solvents, and then suitable ions were added in the form of multivalent cations or polymers with ionic groups. When the pH is above ca. 7.5 for aqueous solutions (or equivalent chemical surroundings in organic solvents), the catechol-groups of the dopamine functionalities form metal-ligand complexes with the ions. If a sufficiently high concentration of polymers is present in the solution, a gel forms within few seconds. The modulus as well as the phase angle of the gel depends on the polymer concentration, on the type of solvent, on the type of ion used as well as on the temperature due to the thermoresponsive nature of the N-isopropylacrylamide in the polymer. If an aprotic solvent is used, the gel can form without ions as well due to hydrogen bonding, while in protic solvents such as water suitable ions are required for gelation. The gels are self-healing rapidly in protic solvents, as long as the bonds are in equilibrium with water, which is the case, as soon as minute amounts of water are in the solvent. Self-healing, measured as recovery of G'(t) and G"(t) from an oscillatory shear pulse with $?_0^{max} = 1000\%$ is achieved via opening of the metal-ligand bonds and reforming of the bonds via intermediate bonding states with water. Typically at 98%

GS6

recovery of G' to the levels before the shear pulse takes only ca. 30 s, being one of the fastest self-healing systems known nowadays. For NIDO5% solutions with B^{3+} as counterion, it was possible to monitor the exact bonding situation by ¹¹B-NMR.

Annual European Rheology Conference 2017

Tuesday Afternoon

Symposium SC

Suspensions and colloids

Organizers: Norbert Willenbacher and Philippe Coussot

Tuesday 13:30 Grand Ball

A generalized frictional and hydrodynamic structural model of semi-dense and dense colloidal suspensions

Joao Maia¹, Arman Boromand¹, Safa Jamali², and Brandy Grove¹

¹Case Western Reserve University, Cleveland, OH 44106-7202, United States; ²Massachusetts Institute of Technology, Cambridge, MA 02139, United States

We perform mesoscopic DPD simulations incorporating both hydrodynamic and frictional interparticle interactions to study the effect of interaction potential on the rheology and structure of dense frictional colloidal suspensions. In particular, we performed a series of viscosity and normal stress measurements in suspensions with different volume fractions and obtained, for the first time, a complete picture of the dynamic state and of the microstructure. We confirmed that N1 for semi-dense suspensions stays negative and grows with shear rate, which is consistent with hydrocluster-induced shear-thickening. We show that CST in colloidal suspensions can be explained solely via hydrodynamics, frictional bonds being transient and negligible to the rheological response. In dense suspensions and close to the jamming transition however, friction is required to obtain DST and replicate the recently experimental findings of a transition from negative to positive N1. We prove that hydroclusters form first at low stresses; this brings the particles together, thus allowing frictional contacts to develop, eventually leading to DST. In addition, when each particle is subject to an average of one frictional contact, N1 reverses its increase but remains negative; at approximately two frictional contacts, a percolating network forms and N1 becomes positive.

Tuesday 13:50 Grand Ball

Associative microgels: structure, phase behaviour and flow properties

Maddalena Mattiello and Michel Cloitre

Soft Matter and Chemistry, ESPCI Paris, PSL Research University, CNRS, Paris 75005, France

Microgels are polymeric micronetworks swollen by a solvent, which are known to share generic properties intermediate between those of hard spheres and polymer coils [1]. Recently significant progress has been made in the microscopic modelling of the structural and dynamical behaviour of concentrated suspensions with repulsive interactions [2]. These systems are used as yield stress additives providing a desired texture or rheology to complex formulations. To improve their efficiency and develop new properties, novel functional microgels with tunable interactions have been invented, which question the role of attractive interactions in soft glasses.

Here we report on a novel class of associative microgels obtained by decorating the surface of the network with hydrophobic macromonomers, able to induce short range attractions among microgels in polar solvent as water. The strength of the interactions is tuned through the composition and architecture of the associative moieities.

Using linear viscoelasticity, non linear rheology, static and dynamic light scattering we establish the dynamical state diagram of associative microgels. The comparison with purely repulsive microgels with exactly the same composition, crosslink density, and particle size highlights the originalities of associative microgels. In the jammed glass regime, in situ flow measurements show that attractive interactions are responsible for flow heterogeneities - a competition between wall slip and/or shear-banding- controlled by the association strength. We propose a two-state model involving two characteristic timescales, associated to relaxation of the associations and cage opening respectively, to rationalize shear banding in these systems.

D. Vlassopoulos and M. Cloitre, Curr. Opin. Coll. Interf. Sci. 19, 561-574 (2014)
 C. Pellet and M. Cloitre, Soft Matter, 2016,12, 3710-3720

Tuesday 14:10 Grand Ball

Simulating large, anisotropic density fluctuations in colloidal gels under shear

James Swan¹ and Zsigmond Varga²

¹Chemical Engineering, Massachusetts Institute of Technology, Cambridge, MA, United States; ²Massachusetts Institute of Technology, Cambridge, MA, United States

The steady shear of weak colloidal gels results in vorticity aligned density fluctuations. These have been measured in neutron scattering and flow dichroism experiments and observed with microscopy coupled to rheometer tools of varying geometry. The origins of this instability remain a mystery, and discrete element simulations of colloidal gels have to date, failed to reproduce the phenomena. We use new Brownian Dynamics simulations to show that this instability is fluid mechanical in origin, and results from long-ranged hydrodynamic interactions among particles in the gel. Squeeze flows between vorticity aligned flocs prevent mutual collisions and realignment, thus promoting stability of large-scale anisotropic density fluctuations. The nonlinear rheology in sheared colloidal gels and measures of their structural anisotropy determined from simulations agree well with a wide variety of experiments. Finally, we demonstrate collapse of this

data across different shear rates, strengths of interaction, and volume fractions using a single force scale -- the most probable rupture force for the inter-colloid bonds.

Tuesday 14:30 Grand Ball

Non-equilibrium states of attractive colloids under shear

George Petekidis

IESL and Department of Materials Science and Technology, FORTH and University of Crete, Heraklion 71110, Greece

The rheology of non-ergodic states of attractive colloids has been the subject of intense investigation both experimentally and by computer simulations, while theoretical models aim in describing the dependence of their viscoelastic properties on key parameters such as volume fraction and attraction strength. Here we examine fundamental aspects of the linear and non-linear response of such systems, ranging from low and intermediate volume fraction gels to highly concentrated attractive glasses, and compare experimental findings with Brownian Dynamics simulations results. We mainly focus on the way such systems yield under the application of steady or oscillatory shear via startup shear tests and large amplitude oscillatory shear, as well as on the mechanisms of gel reformation and accompanied stress relaxation after shear cessation. We discuss the phenomenology of two step yielding, widely observed experimentally, and the underlying mechanisms and relevant length- and time-scales that cause such behavior and contrast it with findings from computer simulations with and without hydrodynamic interactions. We further report on the types of rejuvenation protocols, either by shear (steady or oscillatory) or by temperature or volume fraction quench, as a tool to either provide reproducible initial states or, more interestingly, to tune the final properties of such non-equilibrium states (gels or attractive glasses).

Tuesday 14:50 Grand Ball

Characterizing the state of partially dispersed colloidal suspensions by high-frequency rheology <u>Bram Schroyen¹</u>, Peter Van Puyvelde¹, and Jan Vermant²

¹Department of Chemical Engineering, KU Leuven, Leuven, Belgium; ²Department of Materials, ETH Zurich, Zurich, Switzerland

Nanoparticle based materials have substantial potential due to novel functionalities associated with the nanoscale. However, to express this functionality the particles need to be well dispersed. The actual morphology of nanodispersions is much more complex than often realized. Previous studies have shown that classical rheological measurements can offer an integrated picture of the dispersion state. To extend the applicability of these techniques high-frequency dynamic measurements are needed to determine the degree of dispersion. The aim of this research is thus the development of a general framework to assess the dispersion quality. A home-built piezo-shear rheometer is developed to extend the dynamic frequency range of classical rheological measurements. Rheological measurements at low and high frequencies are combined to offer a clear view of the dispersion quality. At higher frequencies, the loss modulus G" is dominated by matrix contributions and by hydrodynamic interactions from the particles. In this region the effective volume occupied by the particles or particulate aggregates can be examined even when being part of a network. As such, a quantitative dispersion quality index can be derived for the analysis of different dispersion methods and states.

Tuesday 15:10 Grand Ball

Gravitational collapse of colloidal gels: structure, dynamics, and rheology

Roseanna N. Zia and Poornima Padmanabhan

Chemical Engineering, Cornell University, Ithaca, NY 14853, United States

We investigate the phenomenon of gravitational collapse in colloidal gels via dynamic simulation. In moderately concentrated gels formed via arrested phase separation, rupture and re-formation of bonds of strength O(kT) permit ongoing structural rearrangements that lead to temporal evolution - aging - of gel structure and rheology. The reversible nature of the bonds also allows the gel to transition from solid-like behavior to liquid-like behavior under external forcing, and back to solid-like behavior when forcing is removed. But such gels have also been shown to be susceptible to sudden and catastrophic collapse of the entire structural network, after which the gel sediments into a dense layer, eliminating any intended functionality of the network scaffold. Although the phenomenon is well studied in the experimental literature, the microscopic mechanism underlying the collapse is not understood. To study this behavior, we conduct large-scale dynamic simulation to model structural and rheological evolution in colloidal gels subjected to gravitational stress, examining the detailed micro-mechanics in three temporal regimes: slow, pre-collapse evolution; collapse and rapid sedimentation; and long-time compaction. A range of attraction strengths and gel ages, and their effect on the critical force that triggers collapse, are studied.

Tuesday 16:00 Grand Ball A monodisperse polystyrene melt and a suspension of Brownian particles studied with Anton Paar's

SC12

SC11

partitioned plate geometry CPP8 Thomas Schweizer

Department of Materials, ETH Zürich, Zürich CH-8093, Switzerland

Anton Paar has issued a commercial partitioned plate geometry CPP8 which allows accurate determination of the viscosity and the determination of both normal stress differences as the main benefits. First experiments with a mono-disperse polystyrene melt at 180° C have shown that there is a temperature difference between the two partitions due to temperature control with a convection oven. It is shown how this deficiency is relieved by attaching a booster heater to selectively increase the temperature of the inner partition. The second system studied is a suspension of 100 nm diameter cross-linked PMMA particles (45% by weight) in DOP. This sample shows shear hardening for all reliable shear rates (> 1 s⁻¹). The partitioned plate geometry not only allows for the determination of N₁ and N₂, but also gives two viscosity signals, from the core and the entire sample. These signals show slightly different time dependencies for all shear rates studied (1-

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 100 s^{-1}). Calculated from the two normal force signals, N₁ turns out to be negative beyond a strain of roughly 2, N₂ is negative till a strain of 5 and changes sign thereafter.

Tuesday 16:20 Grand Ball

Wall slip of Yield Stress Fluids

Xiao Zhang¹, Elise Lorenceau¹, Florence Rouyer¹, Julie Goyon¹, Tarik Bourouina², Philippe Basset², and Philippe Coussot¹ ¹Laboratoire Navier, Université Paris-Est, Champs-sur-Marne 77420, France; ²Laboratoire ESYCOM, ESIEE Paris, Noisyle-Grand 93162, France

Suspensions often exhibit wall-slip along smooth surfaces. This effect has a major impact with concentrated suspensions exhibiting a yield stress which can apparently flow under low external stresses, whereas in fact the bulk remains undeformed. In that case the flow occurs as a result of the intense shear of very thin liquid layer between the wall and the bulk. Wall-slip of concentrated suspensions has been extensively studied by Cloitre and Bonnecaze [1-3], who carried out direct observations and rheological measurements with model and developed an elastohydrodynamic theory which apparently well explains the wall slip of microgels and, in a less extent, of emulsions. To continue their work, we investigate the wall-slip of emulsions by performing rheological measurements with parallel plate surfaces and directly observing their flow characteristics in capillaries by MRI measurements. We try to understand, first, the role of the material itself, including the composition (direct/inverse emulsions, surfactants) as well as the concentration of the system, and second, the role of chemical and geometrical (roughness) properties of the smooth surfaces. Globally speaking we observe a strong sensibility of wall slip to these material and surface properties, and several effects that can hardly be understood from the above theoretical frame. In particular, although we distinguish two regimes of dependencies of slip velocity vs shear stress in agreement with this frame, the variation of the slip layer thickness appears to depend on the emulsion type and surfaces. A strong difference of wall slip is also observed between inverse and direct emulsions. Besides, with MRI, we are able to measure the slip velocity when the emulsion bulk is highly sheared, and thus opens a new route to observe wall slip under high external stresses.

J.R. Seth et al. (2012), Soft Matter, 140-148.

J.R. Seth et al (2008) J. Rheol., 1241-1268.

S.P. Meeker (2004) J. Rheol., 1295-1320.

Tuesday 16:40 Grand Ball

Layer-Formation of Non-Colloidal Suspensions in a Parallel Plate Rheometer under Steady Shear Sven Pieper¹, Steffen Jesinghausen², and <u>Hans-Joachim Schmid</u>³

¹Particle Technology Group, Paderborn University, Paderborn, North Rine Westfalia 33098, Germany; ²Particle Technology Group, Paderborn University, Paderborn, North Rine Westfalia 33098, Germany; ³Particle Technology Group, Paderborn University, Paderborn, North Rine Westfalia 33098, Germany

The measurement of a complex fluid's viscosity is frequently impeded by structuring effects and other changes of the microstructure that are induced by the measurement device's geometry. One such effect is the formation of structured layers at the confining surfaces. While layering appears to be a general feature of complex fluids it is mostly neglected for non-colloidal suspensions. The currently available literature on this topic focusses on simulations and experimental work in Couette cells. Only very little is known about the layering behavior in rotational plate-plate geometry since the inhomogeneous shear rate complicates meaningful experimental work. The aim of this work is to characterize the layering of non-colloidal suspensions in a parallel plate geometry as a function of the distance from the axis of rotation. Notably, the development of such layers as a function of the ratio between gap height and particle diameter as well as the influence of the bulk concentration was investigated. A custom built plate-plate system with a circumferential guard ring and optical accessibility was used to perform optical concentration and velocity measurements. The investigated suspension was composed of spherical PMMA particles (100 and 125µm) in a matrix consisting of 54.76 wt% Triton-X100, 25.23 wt% poly(ethylene glycol) 400 and 20.01 wt% of a 60.00 wt% sodium iodine in deionized water solution. The fluid was formulated to match both the density and refractive index of the particles. Thus we obtained suspensions that were sufficiently transparent and had a negligible yield stress. We found that stable layers form at the plates and that the concentration of particles in these layers stabilizes above a certain ratio between gap and particle size. The presence of stable layers, and the inhomogeneity of the concentration over the gap in general, contribute towards the poor transferability of data between different devices. Particle migration models cannot account for these effects at the moment and have to be improved

Tuesday 17:00 Grand Ball

Convection and migration of colloids during exclusion zone formation

Daniel Florea¹, Sami Musa², Jacques M. Huyghe², and <u>Hans M. Wyss¹</u> ¹Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands; ²Biomedical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands

We experimentally study exclusion zone (EZ) formation, a phenomenon where upon contact of an aqueous suspension with a solid surface, the colloidal particles are repelled from the surface over distances as long as several hundred micrometers. While this effect has been observed for decades, its physical origins have remained largely unclear. We have recently shown that the physical origin of EZ formation is a combination of ion-exchange at the surface, diffusion of ions, and *diffusiophoresis* of colloids in the resulting ionic gradients [1].

Here we will discuss experiments, which, in addition to the migration of particles, focus on understanding the convective flows that often appear to accompany EZ formation [2]. We study these flows in detail and show that they are driven by the same ionic gradients that drive exclusion zone formation. Our experiments confirm that the observed behavior is consistent with *diffusioosmosis*, the drift of fluid along a surface, driven by an ionic gradient. Further confirming this, we can control and suppress the convective flows by varying the surface properties of the sample cell.

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Our experiments thus suggest that a full description of the phenomenon of exclusion zone formation needs to take into account the diffusioosmotic flows of fluid near the surfaces. We expect our work to be relevant to applications that exploit exclusion zone formation, for instance in water purification, or advanced separation technology.

[1]: S. Musa, D. Florea, H.M. Wyss, J.M. Huyghe Soft Matter 12, 1127-1132 (2016)

[2]: D. Florea, S. Musa, J.M. Huyghe, H.M. Wyss Proceedings of the National Academy of Sciences 111, 6554-6559 (2014)

Tuesday 17:20 Grand Ball

The continuous modeling of charge-stabilized colloidal suspensions in shear flows

Yannick Hallez, Ioannis Gergianakis, Martine Meireles, and Patrice Bacchin

Laboratoire de Génie Chimique, Université de Toulouse, Toulouse, France

Flows of concentrated colloidal suspensions may exhibit a rich set of behaviors due to both hydrodynamic and colloidal interactions between the particles. Colloidal flows are generally modeled with an effective Navier-Stokes equation and a mass balance for the solid phase involving a diffusion coefficient given by the generalized Stokes-Einstein relation. This picture corresponds to a near equilibrium regime in which entropic and colloidal forces dominate over hydrodynamic interactions, the latter being totally ignored. On the other hand, suspension flows far from equilibrium require the modeling of significant hydrodynamic stresses responsible in particular for shear-induced migration, a phenomenon known to occur in some industrial processes involving colloids, such as ultrafiltration. The choice of the proper model ingredients requires a knowledge of the domains in parameter space in which colloidal or hydrodynamic effects are dominant. In this article, such a phase diagram is established for a channel flow of charge-stabilized colloids with a version of the suspension balance model including both colloidal and hydrodynamic effects at the continuous level. It is shown that the classical Péclet number is not sufficient to characterize the flow regime. The phase boundary between the colloidal and hydrodynamic regimes exhibits an original shape explained by the dependence of electrostatic interactions with the colloidal surface charge, and in particular by the phenomenon of ionic condensation. We also show that the phase diagram can be predicted based on the knowledge of a rescaled Péclet number comparing the hydrodynamic stress scale to the bulk modulus of the suspension. The criterion determined here provides important guidelines for the efficient modeling of colloidal flows.

Reference:

The continuous modeling of charge-stabilized colloidal suspensions in shear flows, Hallez, Y. and Gergianakis, I. and Meireles, M. and Bacchin, P., Journal of Rheology, 60, 1317-1329 (2016)

Tuesday 17:40 Grand Ball

Shear reversal response of frictional suspensions

Frédéric Blanc¹, <u>François Peters</u>¹, Enzo D'ambrosio², Laurent Lobry¹, and Elisabeth Lemaire¹ ¹Université de Nice, LPMC, UMR 7336, Nice, France; ²Université de Nice, Nice, France

Lately, several studies pointed the key role of contact forces in the mechanical response of suspensions of non-Brownian rough spheres in Newtonian liquids. Both particle roughness [1] and frictional contacts [2] strongly increase the suspension viscosity. A Transition from frictionless to frictional contact between particles has been invoked to explain the discontinuous shear thickening in concentrated suspensions [3]. Recent numerical simulations [4] showed that shear reversal experiments, first proposed by Gadala-Maria and Acrivos [5], make it possible to estimate the contribution of contact forces to the viscosity. In this paper, we present the viscosity response to shear-reversal of suspensions made of either faceted sugar particles or PMMA spherical particles in a Newtonian silicon oil. In such a transient shear flow, the viscosity decreases after the shear inversion to a minimum where contacts vanish, and increases again up to the steady value as frictional contacts re-build [4,6].

The steady viscosity and the minimum viscosity were measured for both suspensions as a function of particle volume fraction with the following results. (i) Steady viscosity are larger in sugar particle suspensions than in spherical particle suspensions. (ii) Both suspensions show close values of the minimum viscosity.

We conclude from these experiments that contact forces between particles play a more important role in the steady rheological behavior of sugar particle suspensions than in spherical particle suspensions.

[1] Tanner R. I. & Dai S. (2016). JOR 60, 809-818

[2] Gallier S. et al. (2014). JFM 757, 514-549

[3] Mari R et al. (2014). JOR 58, 1693-1724

- [4] Peters F et al. (2016). JOR 60, 715-732
- [5] Gadala-Maria F. & Acrivos A. (1980). JOR 24, 799-814
- [6] Lin N. Y. C. et al. (2015). PRL 115, 228304

SC17

Symposium NF

Non-Newtonian fluid mechanics and fluid instabilities

Organizers: Natalie Germann and Suzanne Fielding

Tuesday 13:30 Amalienborg Concentration gradient in shear banding wormlike micellar solutions revealed by spatially resolved 1-2 shear SANS and PTV

Lionel Porcar¹, Michelle Calabrese², Matthew Helgeson³, Peng Chen³, and Norman J. Wagner² ¹Large Scale Structures, Istitut Laue Langevin, Grenoble, France; ²Dept. of Chemical & Biomolecular Engineering, University of Delaware, Newark, DE, United States; ³Dept. of Chemical Engineering, University of California, Santa Barbara, CA 93106, United States

Complex fluids known to exhibit the shear banding phenomenon have been studied extensively both experimentally using NMR velocimetry, flow velocimetry, and flow-SANS and SAXS measurements as well as using constitutive modeling methods. The search for the physical origin of shear banding has motivated a theoretical coupling of the shear-induced alignment and fluctuation of surfactant or polymer systems to the nonlinear rheology.

The development of the 1-2 (velocity and gradient plane) shear cell sample environment has enabled spatially-resolved neutron scattering measurements to be taken along the velocity-gradient direction, which can be used to elucidate the shear banding behavior of WLM solutions. Here we present a precise and thorough investigation of surfactant wormlike micelle under shear using a combination of particle tracking velocimetry and neutron scattering. Small angle scattering and transmission measurements using the newly developed 1-2 shear cell with magnetic coupling and with a 0.1mm spatial resolution within 1mm gap size: sample transmission is monitored across the shear gap; high angle scattering measurement is also performed in order to determine the incoherent scattering contribution which is directly related to the surfactant concentration. All these measurements have been performed to a series of samples previously hypothesized to exhibit concentration-coupled shear banding, in order to deduce (or not) surfactant concentration gradient through the shear banding regime. They are discussed in light of the "resolution" of the applied methodology and the nature of the systems to shed light into this important phenomenon of shear banding.

Tuesday 13:50 Amalienborg

Edge fracture instabilities in polymeric fluids

Ewan J. Hemingway, Halim Kusumaatmaja, and Suzanne M. Fielding

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Edge fracture is a free surface instability that can develop when viscoelastic fluids are subjected to large shear-rates in common experimental geometries (e.g., cone and plate). The instability manifests as a crack that propagates inwards from the sample edge, and disrupts rheological measurements. By analysing the linear stability properties of a free surface between a bulk polymeric fluid under shear and the air, we explore the mechanisms that drive the edge fracture instability and characterise the critical shear-rate at which it first appears. These analytics also provide insight into how edge fracture might be avoided experimentally. Our predictions are complemented by full 2D hydrodynamical simulations using a diffuse-interface approach to correctly capture the dynamics of the contact line (where the air/fluid interface meets the solid wall of the rheometer). Finally we comment on the implications of our work for interpreting reported shear-banding instabilities in linear entangled polymer solutions.

Tuesday 14:10 Amalienborg

Non-local stresses in colloidal suspensions: modeling and simulation

Howon Jin¹, Kyong-ok Kang², Kyung Hyun Ahn¹, Wim J. Briels², and Jan K. G. Dhont²

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Spatial variations of the shear rate and/or density give rise to so-called non-local stresses, which add to the common stress that corresponds to the local shear rate and density. These non-local stresses play an important role in, for example, shear-banding instabilities where there are large spatial gradients within the interface between shear-bands, and in micro-fluidic devices where large gradient exist due to small-scale confinement. So far, these stresses have been introduced phenomenologically. One way to incorporate non-local stresses is through the introduction of the "shear-curvature viscosity" (Dhont, 1999), which results from a formal gradient expansion of the stress tensor up to second order spatial derivatives in the shear rate. In this presentation, we discuss a microscopic approach and express the shear-curvature viscosity in terms of the inter-particle interaction potential and the shear-distorted pair-correlation function. In the modeling part of this work, a systematic gradient expansion of a general expression for the stress tensor that is valid under non-uniform flow field conditions (Dhont and Briels, 2002) is performed up to the desired order. An expression for the shear-curvature is thus obtained in terms of the hydrodynamic forces density on the surface of the colloids embedded in an inhomogeneous flow field. These force densities can be calculated analytically, giving rise to an explicit expression for the shear rate. Numerical values for the pair-correlation function are obtained from Brownian Dynamics simulations on homogenous systems. Brownian dynamics simulations are also performed for inhomogeneously sheared systems, with a spatially sinusoidally varying flow field, from which the non-local stress is obtained. These simulation results are compared to the theoretical predictions.

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Tuesday 14:30 Amalienborg

Numerical investigation of shear banding polymer solutions in benchmark flows Soroush Hooshyar, Mohamadali Masoudian, and <u>Natalie Germann</u>

TUM, Freising, Germany

Shear banding is a phenomenon observed in soft materials, such as polymer solutions. We present a new two-fluid model for semi-dilute entangled polymer solutions that was recently developed using the generalized bracket approach of nonequilibrium thermodynamics [1]. In the two-fluid framework formulated by Germann et al. [2-3], the local concentration and viscoelastic stress gradients generate nontrivial differences between the velocities of the microstructural constituents of the solution. The advantage of this framework is that the differential velocity is treated as a state variable, which simplifies the formulation of slip boundary conditions. To obtain an overshoot of the shear stress during the start-up of a simple shear flow, we added the Giesekus relaxation to the conformation tensor equation. In addition, we included a nonlinear relaxation term to capture the upturn of the flow curve at high shear rates. This term is a nonequilibrium thermodynamic reformulation of the term used in the Rolie-Poly model that accounts for convective constraint release and includes chain stretch. To generate smooth and unique profiles, we added a new stress-diffusion term to the time evolution equation of the polymer conformation. In this talk, we will discuss the model behavior in a cylindrical Couette flow [1], a Poiseuille channel flow [4], and a 4:1 contraction flow. To illustrate how to account for the slip in our two-fluid framework, we will utilize the linear Navier slip model [5].

References:

[1] S. Hooshyar and N. Germann. Phys. Fluids., 28, 063104 (2016).

[2] N. Germann, L. P. Cook, and A. N. Beris. J. Non-Newt. Fluid Mech., 207, 21-31 (2014).

[3] N. Germann, L. P. Cook, and A. N. Beris. J. Non-Newt. Fluid Mech., 232, 43-54 (2016).

[4] S. Hooshyar and N. Germann. J. Non-Newt. Fluid Mech., under revision. [5] L. L. Ferrás, A. M. Alfonso, M. A. Alves, J. Nóbrega, O. S. Carneiro, F. T. Pinho. J. Non-Newt. Fluid Mech., 214, 28-37 (2014).

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Relaxation dynamics and apparent local viscosity in the shear banding regime of concentrated wormlike micelles

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Shear banding, i.e. the coexistence of bands with different shear rates and microstructure in simple shear flows has been an important research focus in the past 25 years. However, while modeling suggests that the different bands possess different viscosities, no experimental confirmation of this phenomenon has ever been given.

Using a multispeckle scattering setup installed on a Couette cell mounted on a rheometer, we investigate the shear banding phenomenon in a concentrated wormlike micelles solution. Velocity and birefringence profiles, microscopic relaxation dynamics and macroscopic rheometry are determined simultaneously. Below the shear banding regime, we observe, as expected, a homogeneous shear flow with birefringence following the stress optical rule. Interestingly, the microscopic relaxation curves display two different times scales, the slow characteristic time remaining constant like the viscosity, while the fast one decreases with increasing shear rate and birefringence. This result could be interpreted as an anisotropy of the diffusion coefficient of the suspended particles, and hence of the viscosity of the solution.

In the shear banding regime, we observe that not only the velocity and birefringence fields are spatially heterogeneous, but also the spatial distribution of relaxation times. Further, in this regime a non-negligible radial velocity component exists, and the viscosities deduced from our microscopic measurements do not comply with the lever rule. Those results are discussed in the light of classical shear banding and elastic instabilities hypotheses.

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Shear banding in large amplitude oscillatory shear (LAOStrain and LAOStress) of soft glassy materials Rangarajan Radhakrishnan and <u>Suzanne M. Fielding</u>

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We present recent results concerning shear banding in soft glassy materials (dense colloids, foams, emulsions, microgels, etc.) subject to large amplitude oscillatory shear flow (LAOS), considering both LAOStrain and LAOStress. In particular, we discuss numerical simulations of the widely used soft glassy rheology model, within which we demonstrate strong shear banding over an extensive range of amplitudes and frequencies of the imposed shear rate (or stress). Crucially, this is true even in materials that have a monotonic underlying constitutive curve for stationary homogeneous flow, and so do not show banding as their steady state response to a steady imposed shear flow. Counterintuitively, we show that this banding persists in LAOS even in the limit of zero frequency, where one might a priori have expected a homogeneous flow response. We explain this behaviour in terms of an underlying alternating competition, within each imposed cycle, between glassy aging and flow rejuvenation. Our predictions have potentially important implications for the flow behavior of aging yield stress fluids, suggesting that shear banding might generically be expected in flows of even arbitrarily slow time variation. Finally, we demonstrate that the presence of banding has a strong effect on the shape of the Lissajous-Bowditch curves. We therefore counsel caution to theorists seeking to compute LAOS response within calculations that impose upfront a purely homogeneous flow.

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Tuesday 16:00 Amalienborg

Viscoelastoplastic & thixotropic predictions for sharp-corner contraction-expansion circular flows with time-dependent constitutive equations

<u>Michael F. Webster</u>¹, J. Esteban López-Aguilar¹, Hamid Reza Tamaddon-Jahromi¹, and Octavio Manero² ¹College of Engineering, Swansea University, Swansea SA1 8EN, United Kingdom; ²Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico City 04510, Mexico

In this predictive modelling finite volume/element study, with enhanced numerical stability features, a comparative analysis is performed for time-dependent and viscoelastoplastic constitutive equations, in a circular contraction-expansion geometry of high aspect ratio, 10:1:10. A revised micellar $BMP+_tp$ model is proposed, which reflects a bounded extensional viscosity response and an N_{1Shear} -upturn (lost in earlier model-variants). Such a $BMP+_tp$ model is contrasted against a counterpart De Souza model via flow-structure and yield-front representation. The *plastic regime* is studied at low flow-rates (Q) and for extremely concentrated fluids. In this, elasticity-increase causes asymmetry about the contraction-plane, whilst yield-stress and enhanced strain-hardening promote solid-like features, apparent through augmented unyielded regions and rising pressure-drops. Concerning *viscoelastic response* (at larger-Q; minimising plasticity influence), vortex-structures reflect a complex interplay between the pure-extensional centreline-flow and the pure-shear flow deformation along walls and in recirculation-zones. The extensional-deformation observed correlates with expected hardening in uniaxial extension, whilst the activity within the vortex-cell correlates with normal stress response in shear. The influence of strain-hardening/softening is reflected through the evolution in size of the upstream-vortex. With *Q-rise*, the upstream vortex-centre loci are observed to switch between that of a symmetric salient-corner vortex to an elastic corner-vortex. Then, beyond the strain-hardening phase, when softening occurs, asymmetric salient-corner vortices are recovered. For strong-hardening regimes and solvent-dominated fluids, an intermediate *lip-vortex-formation* phase is noted, alongside coexistence with the salient-corner vortex. Such a vortex-coexistence phase is distinctly absent in polymerconcentrated fluids.

Tuesday 16:20 Amalienborg

Dynamics of thin sheets of complex fluids and ultrasoft solids freely expanding in air Srishti Arora¹, Serge Mora², Christian Ligoure³, and <u>Laurence Ramos</u>⁴

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We investigate the dynamics of thin sheets freely expanding in air. The sheets are produced by impacting a drop onto a small target or onto a cushion of liquid nitrogen, in order to suppress any dissipation process. To disentangle the role of capillary, viscous and elastic forces in the dynamics of the sheets several materials are used, whose rheological characteristics are tuned over several orders of magnitude: viscous liquids, viscoelastic Maxwell fluids characterized by an elastic modulus, G0, a relaxation time, T, and ultrasoft solids with elastic modulus as low as 10 Pa. For viscoelastic fluids, when T is shorter than the typical lifetime of the sheet (~ 10 ms), the dynamics of the sheet is similar to that of Newtonian viscous liquids with equal zero-shear viscosity. In that case, the maximal expansion of the sheet, dmax, decreases with the viscosity and can be quantitatively accounted for by a model based on the viscous dissipation on the target. On the other hand, when T is longer than the typical lifetime of the sheet, the behavior drastically differs. The sheet expansion is strongly enhanced as compared to that of viscous samples with comparable zero-shear viscosity, but is heterogeneous with the occurrence of cracks, revealing the elastic nature of the viscoelastic fluid. By contrast, sheets produced with ultrasoft solids expand but never break. Furthermore, we demonstrate that the surface tension of the soft elastic drops must be taken into account in order to successfully model their expansion. Overall, we have rationalized the spreading of sheets for viscous, viscoelastic and elastic materials by taking into account surface tension, elastic deformation and viscous dissipation.

Tuesday 17:00 Amalienborg

Statistical description of elastic turbulence in the Taylor-Couette flow of micellar solutions

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We perform a statistical characterization of a fully-developed elastic turbulent regime displayed by wormlike micellar solutions under steady shear flow. By combining conventional rheometry with a visualization technique into a Taylor-Couette cell, we are able to get simultaneously the global and local response of the fluid. We study the influence of the route to turbulence on the statistical features of the turbulent state. We focus on a shear-banding micellar system, CTAB-NaNO₃ at [0.3-0.4] M, which exhibits a sudden laminar-to-turbulent flow transition (with no intermediate flow pattern). The spatio-temporal dynamics of this system display anomalous scaling properties. We next provide a qualitative comparison with a non-shear-banding micellar solution (CTAB-NaNO₃ at [0.1-0.3] M) for which a wavy-vortex flow precedes the turbulent flow.

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Tuesday 17:20 Amalienborg

Active and hibernating turbulence in viscoelastic plane Couette flows

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We analyse the active and hibernating turbulence in drag reducing plane Couette flows using direct numerical simulations of viscoelastic FENE-P fluids. The polymer turbulence interactions are studied from an energetic standpoint for a range of Weissenberg number, fixing the Reynolds number, the viscosity ratio and the maximum polymer molecule extensibility. The qualitative picture that emerges from our energy budget and spectral analyses is a cycle which begins when the polymer-flow interactions in the active turbulence regime favour the extension of the molecules. In their stretching process, polymers reduce the mean fluid velocity and partially suppress the turbulent structures (the small-scale ones), driving the flow towards a very weak turbulent hibernating regime in which the polymers tend to relax. Hence, their level of stretching decreases while a significant amount of polymeric energy is released into the flow, increasing its mean velocity towards the Maximum Drag Reduction asymptote. Additionally, a significant part of the polymeric energy is directly injected into the fluctuating velocity field, favouring the re-activation of turbulence. Finally, the active turbulence again stretches the molecules, reinitiating the cycle.

Tuesday 17:40 Amalienborg

Experimental investigations of the elasticity influence on the Kelvin-Helmholtz instability

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The present study is concerned with the experimental investigation of the onset of the Kelvin-Helmholtz instability at the interface between a Newtonian fluid and a viscoelastic polymer solution. The aim of the work is to investigate the elasticity influence on the hydrodynamics in the vicinity of the interface formed between two immiscible fluids in a concentric cylinders configuration. In particular, the authors establish the correlation between the elasto-capillary number and the wave number associated with the onset of the Kelvin-Helmholtz instability. The experiments are performed using the Paar-Physica MC 301 rheometer as platform for different concentric cylinders set-ups. The inputs in the tests are different ramps in rotational velocity for the inner cylinder, the transparent outer cylinder being at rest. The direct visualizations of the interface's dynamics are correlated with the frequency of a high resolution stroboscopic lamp. The Newtonian samples are silicon oils and mixtures of glycerine in water; the viscoelastic liquids are solutions of different PAA concentrations in water

Symposium SM

Polymer solutions and melts

Organizers: Giovanni Ianniruberto and Qian Huang

Tuesday 13:30 Christiansborg

Extensional viscosity of unentangled polymer melts

Yumi Matsumiya and Hiroshi Watanabe

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Uniaxial extensional behavior was examined for unentangled Polystyrene (PS; M = 27k) and Poly (tert-butyl styrene) (PtBS; M = 53k) with a commercially available filament stretching rheometer, VADER 1000. At sufficiently high stretching rates, strain hardening was observed in viscosity growth function of both PS and PtBS, in particular for PtBS. Stress relaxation just after stretch to Hencky strain of 3 was also examined. Relaxation time was insensitive to stretching rate when the Weissenberg number *Wi* defined with respect to rate the terminal relaxation rate in the linear regime is smaller than unity, whereas the initial relaxation (just after cessation of stretching) was considerably accelerated when *Wi>* 1. This result is consistent with previously reported results for entangled PS chains, where the initial Rouse relaxation was accelerated under fast stretch. Thus, the reduction of monomeric friction under stretching at high *Wi* plays a significant role in uniaxial extensional behavior of the polymer irrespective of entanglement.

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Dynamic dilution - a key element in modeling extensional viscosity of linear and LCB polymers

Manfred H. Wagner and Esmaeil Narimissa

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A novel Hierarchical Multi-mode Molecular Stress Function (HMMSF) model for linear and LCB polymer melts has been presented, which implements the basic ideas of (i) hierarchical relaxation, (ii) dynamic dilution, and (iii) interchain tube pressure. The modelling is solely based on the linear-viscoelastic relaxation modulus with only one non-linear material parameter, the dilution modulus. The model is assuming that chain stretch results from a tube diameter which decreases with increasing deformation. A decreasing tube diameter in turn leads to an increasing interchain tube pressure, which limits stretch. Through hierarchical relaxation, dynamic dilution results in larger tube diameters of chain segments with longer relaxation times, which increases the potential of these modes for larger stretches. The onset of dynamic dilution occurs when the relaxation process has reached the dilution modulus. The relaxation times in combination with the

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dilution modulus determine the magnitude of strain hardening, which is enhanced by long relaxation times and narrow molecular weight distribution. This is exemplified by metallocene catalysed polymers with star molecules featuring only one branch point: Due to their narrow molecular weight distribution, there is less dilution by oligomers, and the dilution modulus is larger, leading to enhanced strain hardening. The HMMSF model demonstrates excellent qualitative and quantitative agreements with the uniaxial extensional viscosity data of polydisperse linear as well as long-chain branched polymer melts for a wide range of strain rates based solely on the linear-viscoelastic relaxation modulus with only one free non-linear parameter, the dilution modulus.

Tuesday 14:10 Christiansborg

Friction reduction explains data of extensional startup and relaxation for PS melts and solutions

Gunwoo Park and Giovanni Ianniruberto

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The uniaxial extensional-flow data of Huang and coworkers [ACS Macro Letters 2013, 2, 741; Journal of Rheology 2016, 60, 465] on several polystyrene systems, both melts and solutions, are here successfully compared with the predictions of a recent model [Ianniruberto, Macromolecules 2015, 48, 6306] that accounts for flow-induced friction-reduction effects. Comparison with the solution data [ACS Macro Letters 2013, 2, 741], only differing for the size of the oligomeric solvent, confirms that friction reduction must include nematic interactions between the oligomeric solvent and the polymer molecules, at least for sufficiently long oligomers. The stress relaxation data following fast uniaxial extension, recently reported by Huang and Rasmussen [Journal of Rheology 2016, 60, 465], confirm that the short-time relaxation process occurs at a faster rate because of the friction reduction induced by the previous flow.

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Experimental investigation of entrance effects in the pressure flow of high molar mass polymer through short dies: a viscoelastic approach

Salvatore Coppola and Federico Sebastiano Grasso

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Entrance effects are of particular importance when analyzing pressure flow of polymer melts in short dies (i.e. with Length/Diameter, L/D, not far from unity) as they might significantly affect both flow stability and die swell, especially if highly elastic polymer melts are considered. In this work, we made use of capillary rheometry adopting a number of capillary dies with different diameters and L/D ratios. It was so possible to apply different extensional rate conditions at the die entrance and to check on the occurrence of wall slip. We decided on purpose not to apply to our data any of the typical pressure corrections. Most corrections indeed analyze the entrance flow problem from a "purely viscous" viewpoint and deal with entrance pressure as if it was just an extra loss of mechanical energy. Instead, we partly follow Malkin et al.'s approach [J. Rheol. (2014)] of considering pressure losses as a unique function of material residence time inside short channels. Differently from Malkin et al., we find out that apparent shear stress is NOT a unique function of average residence time in the capillary die. Still, as we believe that Malkin et al.'s "viscoelastic" approach is in principle appropriate for highly elastic polymer melts but somehow ineffective for our material, we propose a simple but physically sound extension of Malkin et al.'s approach. We show that for materials, like ours, with relaxation times much longer than their average residence time inside the die, the extensional deformation starting upstream in the reservoir is not negligible. In fact, we estimated that, differently from Malkin et al.'s samples, in our case just a small amount of that extensional stress is relaxed before the material enters the die channel. In conclusion, from a viscoelastic viewpoint, we considered an extra residence time in order to take into account the deformation occurring upstream in the reservoir. With such an expedient, we were able to build a mastercurve of apparent shear stress versus global residence time.

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Coarse-grained approach for fast shear flow of soft matter fluids in the bulk melt

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Our main goal is to provide insight on the non-linear shear rheology of entangled polymer chains. More specific, we would like to identify the molecular origin of the stress overshoot as well as to thoroughly understand how chain retraction and disentanglement are influenced by the deformation rate and the chain topology (e.g. linear or star chains). As a first step, we compare the predictions of two different tube models, namely the Rolie-Poly [1] and the Mead-Larson-Doi [2] (MLD) models, against experimental data on Poly-hydroxybutyrate (PHB) melts of linear topology[3]. Both aforementioned models incorporate the molecular mechanisms of reptation, chain stretch, chain retraction, and convective constraint release. To examine how chain retraction and disentanglement are influenced by the chain of topology, we consider the non-linear response of star polymers. We make appropriate modifications to the Rolie-Poly and MLD models, such as suppression of chain reptation and incorporation of arm retraction, as to compare their predictions against shear start-up data of 3-armed and 6-armed PHB chains[3]. We comment on the performance of the models; we also highlight similarities and/or differences, which we explain in terms of the underlying molecular physics and the way the latter have been implemented in the models.

1: A.E. Likhtman, and R.S. Graham. J. Non-Newtonian Fluid Mech. 114 (2003) 1-12. 2: D.W. Mead, R G. Larson, and M. Doi. Macromolecules 31 (1998) 7895-7914. 3: T. Ebrahimi, S.G. Hatzikiriakos, and P. Mehrkhodavandi. Macromolecules 48 (2015) 6672-6681.

Tuesday 15:10 Christiansborg

Evaluation of tube theories for linear entangled polymers in simple and complex flows

Stylianos Varchanis, Yannis Dimakopoulos, and John Tsamopoulos

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We investigate the capability of two constitutive models (Marrucci & Ianniruberto [1], Rolie-Polie [2]) to predict homogeneous and inhomogeneous flows of linear entangled polymers. The predictions of these tube models are compared to those of two more often used models: one derived from network theory [3], and the other one based on configuration-dependent molecular mobility [4]. Initially we test each single-mode model in rheometric flows of a monodisperse polystyrene solution. When adding the effect of finite chain extensibility factors on the M&I and Rolie-Polie models, it is predicted that it may lead to spurious solutions. Then, two benchmark problems are examined: the unsteady channel flow of a commercial polystyrene melt, and the steady 7:1 contraction-expansion slit flow of a linear polydisperse polyethylene melt. The multi-mode relaxation spectra of the samples are common for all models, while each model's nonlinear material parameters are fitted to simple shear and uniaxial elongation experiments. The finite element method is used to solve the governing equations in 1D and 2D domains. The principal stress difference profiles as well as the predicted pressure drops or flow rates are directly compared to experimental observations [5, 6]. The single mode tube models are found to be superior to PTT and Giesekus models in describing rheometric flows. However, when multimode approximation is considered, all models quantitatively capture the characteristic features of each flow, also achieving a very good agreement with the experimental data.

1. Marrucci G, Ianniruberto G (2003) Phil. Trans R Soc Lond A, 361:677-687 2. Likhtman A., Graham R. (2003) JNNFM, 114:1-12 3. Phan-Thien N., Tanner R., (1977) JNNFM, 2:353-365. 4. Giesekus H., (1982) JNNFM, 11:69-109. 5. Isayev A., (1984) J. Rheol. 28:411 6. Hassell D., Auhl D., McLeish T., Mackley M., (2008) Rheol. Acta, 47:821-834

Tuesday 16:00 Christiansborg

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Diffusion Mechanisms of Very Long Macromolecular Chains: Application to UHMWPE Sintering <u>Tiana Deplancke¹</u>, François Rousset², and Olivier Lame¹

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Manufacturers are constantly looking for new materials that exhibit high wear and impact resistance, especially for uses such as total joint implants or body armors. UHMWPE can meet these requirements. However, the high molecular weight of UHMWPE gives a very high viscosity to the melt and makes it impossible to be processed by conventional techniques such as injection molding or extrusion. As a consequence, the UHMWPE sintering process has been developed. The diffusion of very long chains is generally described by the reptation theory. However, studies have shown that another phenomenon called "melting explosion" permits re entanglements in less time than required for reptation. This can be explained by the high crystallinity and the high melting temperature of the UHMWPE nascent powder that have been assigned to non-equilibrium chain conformations. Nevertheless, this "melting explosion" phenomenon is not sufficient to provide a homogeneous sintered material at the equilibrium state in terms of mass between entanglements. In the present work, we investigate the diffusion of very long chains of polymers, in the case of a molecular weight of 3.9 Mg/mol, by means of rheology experiments. These experiments have been performed in a broad range of temperatures corresponding to the broad rubbery plateau of this material: extend from the melting temperature (140 °C) to the flowing temperature (more than 300 °C). We suggest to describe the macromolecules diffusion mechanisms through a modelization based on thermal activated reptation theory. These results could be used to determine a sintering rate as a function of the processing parameters, i.e. temperature and duration.

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Effects of intermolecular interactions on the viscoelastic behaviour of polyamide melts

Ana R. Martins, Anthony Bocahut, and Paul Sotta

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The effect of the strength and density of interactions on the dynamics of polyamides in the molten state was studied. The interaction strength was varied by introducing functional polar groups on isophthalic acid-based polyamide (PA 6I) backbone. We have studied PA6I, PA 6HIA and PA 6LiSIPA. When compared to PA6I, PA 6HIA has an additional OH group on the phenyl ring capable of forming hydrogen bonds with amide groups, with an estimated energy higher than that of standard amide-amide interaction. PA 6LiSIPA was used as a copolymer with PA6I in a ratio of 95/5, 90/10 and 85/15 molar. All polyamides were amorphous (due to the isophthalic acid, substituted or not) and end-blocked to avoid post-condensation during rheological measurements. For PA 6I, as MW increases, a clear rubbery plateau appears and the longest relaxation time is shifted to lower frequencies. The reference temperature used to shift master curves was chosen to be Tg for all polymers, so that all master curves overlap in the glassy region. The Tg's at which all curves overlap coincide with the values determined by DSC within 2°C. The first noticeable effect of interactions is the increase in Tg by 10 to 40°C. For the same MW, master curves of PA 6I and substituted polyamides overlap in the complete range of frequencies when using an appropriate reference temperature. The rheological master curve of PA 6HIA was taken at Tg +5°C so that it overlaps with the one of PA 6I in the glassy regime. For the copolymer, the master curve also overlaps when choosing as reference temperature Tg+3, Tg+5 and Tg+8°C for 5, 10 and 15% of ionomer. Polyamides with MW lower than entanglement molecular weight were fitted using the Rouse model for polydispersed polymers. Terminal regions of the dynamic moduli were well represented by this model. To conclude, there is no effect of interactions on the general shape of the dynamic moduli, apart from Tg shift and width of the glass transition.

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Open-celled foams based on a polystyrene-block-poly(4-vinylpyridine) diblock copolymer

Maria Schulze, Ulrich A. Handge, and Volker Abetz

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The properties of polymer foams are strongly influenced by the properties of the polymer components and the foam morphology. Opencelled foams can be used in a variety of applications ranging from food packaging to membrane technology. Block copolymers combine the properties of different chemical blocks and consequently allow for tailoring the properties of polymer foams. In addition, the phenomenon of microphase separation can be used for the preparation of foams which are structured on the nanometer scale. In this study, we elucidate the potential of a polystyrene-block-poly(4-vinylpyridene) diblock copolymer for preparing open-celled foams. The technique of batch foaming using water and carbon dioxide as blowing agents is applied for foam preparation. The diblock copolymers were synthesized using the technique of anionic polymerization. In small amplitude shear oscillations, the storage modulus of the diblock copolymer at low frequencies is associated with a solid-like plateau which is caused by the microphase-separated structure. In stress-growth experiments with a constant shear rate, the steady-state viscosity decreases with shear rate (structure-viscous behaviour). Our elongational experiments show that the diblock copolymers of this study are associated with the phenomenon of strain-softening. The transient extensional viscosity in simple elongation agrees with the threefold of the shear viscosity. Our batch foaming experiments reveal that open-celled polymer foams using water and carbon dioxide as blowing agents can be prepared at appropriate processing conditions.

Tuesday 17:00 Christiansborg

Molecular Picture of Effective Local Concentration in Miscible Polymer Blends Chen-Yang Liu¹, Zhi-Chao Yan¹, and Zuowei Wang²

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A complete molecular picture of the effective local concentration (φ_{eff}) in miscible polymer blends is presented, in which the local packing inside the characteristic frictional volume with dimension of Kuhn length l_{K} is considered deliberatively. For polymer solutions, a transition of $\varphi_{\rm eff}$ from the average concentration to the mean intrachain concentration is observed at $I_{\rm K}$, since no segment of surrounding chains can enter the correlation blob centered at the test chain segment. For miscible blends, a correction term is introduced to the existing theoretical model in calculating φ_{eff} by taking into account the fact that the interchain contribution exists only above the overlap concentration of the test polymer component. Moreover, a universal dependence of the self-concentration on the polymer chain stiffness and monomer bulkiness is revealed by scaling analysis and confirmed by comparing with experimental data collected in Literature. Lastly, we demonstrate that the temperature-dependent distribution of ϕ_{eff} due to local concentration fluctuations is controlled by the temperature dependence of the Flory interaction parameter.

Tuesday 17:20 Christiansborg

Morphology stabilization in concentrated blends of PP and PE

Sylvie Vervoort¹, Krischan Jeltsch², and Ewa Tocha³

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Blends of polypropylene (PP) and polyethylene (PE) are of high industrial relevance. They are found in car bumpers, transparent containers or sports goods, e.g.. Many plastic waste recycle streams are also mixtures of various types of PP and PE. In polymer blend applications, the manufacturer strives to reach optimal end-use properties such as mechanical performance, optical properties or chemical resistance. Blend morphology is a determining factor to all these properties. Therefore, morphology control is a key aspect for the use of immiscible polymer blends. It is well-known that fine dispersions can be created when the viscosity ratio in a blend is close to 1 and the probability of droplet coalescence is lower in dilute systems. The blend ratios in practical applications, however, are typically high and the viscosity ratios are not close to 1, which makes it more challenging to create fine morphology features during the blending process. Blends of PP with different types of PE were investigated at blend ratios up to 40 wt% minor phase. As the amount of dispersed phase increased, the blend morphology changed from a droplet-in-matrix system to a co-continuous system. In both cases, the addition of a block copolymer compatibilizer lead to finer morphology features. At higher concentrations of dispersed phase, the typical Palierne analysis of blend rheology did not hold anymore. The difference between predicted and actual measured blend rheology is expected to give information on the blend morphology. Effects of blend ratio, viscosity ratio and compatibilizer addition on morphology and morphology stability will be discussed as well.

Tuesday 17:40 Christiansborg

Bo Lu, Khalid Lamnawar, and Abderrahim Maazouz

polymer systems

Ingénierie des Matériaux Polymères, CNRS, UMR 5223, INSA Lyon, Université de Lyon, Villeurbanne 69621, France

Rheological and dynamic insights into the in situ reactive interphase with graft copolymer in multilayered

We provided rheological and dynamic insights into the role of in situ reactive interphase with graft copolymer in multilayered polymer systems using a polyamide-6 (PA6)/maleic anhydride grafted PVDF (PVDF-g-MAH) bilayer as model. Firstly, influence of the reactive interphase on shear and extensional rheology was studied. The in situ generated interphase by coupling reactions in bilayers significantly contributed to overall viscoelastic responses in both linear and nonlinear regimes. In contrast to start-up shear, shear stress relaxation and extensional rheology were demonstrated to be pretty sensitive to the reactive interphase. Specifically, under fast extensional flows, the reactively healed bilayer showed an enhanced strain hardening mainly due to the in situ formed graft copolymers in interphase. Secondly,

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evolution of reactive interphase and its effects of on microscopic dynamics and structural properties were further probed by dielectric relaxation spectroscopy (DRS). Interestingly, the reactive interphase drastically altered the dielectric responses of the bilayer upon healing, manifesting in the distinct interfacial relaxation/polarization. Relaxation strength of the interfacial polarization was increased linearly as a function of reaction time, and further improved by increasing the number of layers. In good agreement with rheology, DRS also demonstrated the retarded microscopical dynamics by reactive interphase in healed bilayer. Taking the molecular relaxation spectrum as a probe for the structure, effects of reactive interphase on resulting structural properties of bilayers were further evaluated from a dielectric point of view. These findings are aimed at uncovering the effects of reactive interphase on rheology, dynamics, structural and dielectric properties to guide future controlling interface/interphase in multilayered polymer structures and further applications.

Symposium FB

Food and biorheology

Organizers: Henrik Kragh and Ulf Andersen

Tuesday 13:30 Fredensborg

Extensional viscosity of a ß-glucan concentrate

Kristina Karlsson¹, Marco Berta², Camilla Öhgren², Mats Stading², and Mikael Rigdahl¹

¹Polymeric materials and composites, Chalmers university of technology, Göteborg, Sweden; ²Soft Materials Science, RISE Life Science, Gothenberg, Sweden

Today there is an obvious interest and trend towards replacing fossil-based polymers in products of different types with materials based on renewable and sustainable raw materials. One promising route is to extract biopolymers form side streams of agricultural processes. Before a material can be considered as a promising candidate for further processing, a thorough investigation of the rheological properties is required. A fibre fraction from barley processing with β-glucan and starch as major components and protein and arabinoxylan as minor components, was plasticized with water. The rheological properties of suspensions and melts of this fibre fraction were evaluated using capillary viscometry. By subjecting the material to a contraction flow through a hyperbolic die (giving a constant extensional strain rate) while recording the pressure drop, the extensional viscosity of the suspension/melt could be determined, including its temperature-dependence. The composite material was initially mixed with 50 % water at two different temperatures (30 °C and 90 °C) and the microstructure was evaluated by microscopy. Finally, the mechanical properties of cast films of the material were determined using tensile testing. All films were conditioned to different fixed moisture contents before testing.

Tuesday 13:50 Fredensborg

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The elongational behaviour of dysphagia-designed products in the presence of salivary alpha-amylase solutions

<u>Mihaela Turcanu</u>¹, Nadja Siegert², Lucia Frau Tascon², Sebastien Secouard², Edmundo Brito de la Fuente², Corneliu Balan¹, and Crispulo Gallegos²

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Dysphagia is a highly prevalent clinical condition related to any dysfunction that impairs the safe delivery of food and drinks during swallowing. In the last years, many studies have been dedicated to the shear rheology of dysphagia-designed products (DDP) and to the interaction of the bolus with salivary a-amylase, since shear viscosity plays an important role in food oral processing. It is now assumed that extensional rheology may also play an important role in the development of DDP, since food bolus may undergo elongational deformations during the swallowing process. Techniques such as multiple extrusion cell and contraction flows have been used for the investigation of elongational properties of food-products during swallowing. In this work, DDP were studied by means of a capillary break-up extensional rheometer (CaBER) with an attached high-speed camera (Photron Fastcam Mini UX100). Different commercially available fluids were tested, both pure and mixed with reconstituted salivary a-amylase fluid (SAA). The filament breakup time and the filament shape were both qualitatively and quantitatively compared. Furthermore, shear tests were performed by using conventional and an ad-hoc mixing geometries for a complete rheological characterization and definition of dysphagia stages, according to current guidelines. The results obtained provide a first view of the impact of SAA on elongational properties of DDP containing different types of thickener, differentiating between gumbased (GB) and starch-based (SB) when considering the filament shape and its lifetime. It was observed a drastic decrease in filament breakup time of SB-DDP in the presence of SAA, while GB-DDP showed a more constant filament breakup time, regardless of the presence of SAA. Capillary break-up rheometry has been found to be a quick and sensitive method to characterize the structure changes and the elongational properties of DDP in the presence of a-amylase, which could have a significant importance in aspects related to swallowing safety.

Tuesday 14:10 Fredensborg

Comparison of the LAOS Behavior of the Two Main Gluten Fractions: Gliadin and Glutenin

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Crude gliadin and glutenin fractions were extracted from hard red winter wheat flour (14.64% moisture, 33.5% wet gluten, 61.5% water absorption) using the Osborne method with 70% ethanol, were freeze-dried and mixed with 1:1 w/v (g/ml) water. LAOS measurements were carried out with DHR-3 Rheometer at 25 °C at three different frequencies (20, 10, 1 rad/sec) between the strain values of 0.01- 200%. The beginning of non-linearity for glutenin occurred at ~2.5%, while an intial region of strain hardening was observed for gliadin (2.5-10%) at 1 rad/sec frequency and upto 15% at the higher frequencies applied. Lissajous curves showed in the elastic analysis of both fractions glutenin was more elastically dominated since Lissajous curves were narrower, while for gliadin the ellipses were much broader suggesting more fluid-like behavior and each ellipse depended on the magnitude of frequency. Decreasing frequency increased the viscous behavior of both glutenin and gliadin in the non-linear region, but the change in gliadin was much more pronounced. Chebyshev coefficients showed that gliadin and glutenin showed strain stiffening and shear thinning behavior in the non-linear region at the highest frequency applied. However, gliadin showed a decrease in the strain stiffening character after the strain value of 110%. In the lowest frequency applied, glutenin showed shear thickening, where gliadin still showed shear thinning at 200% strain in the non-linear region. The fact that with gliadin, the e3/e1 and v3/v1 showed a maximum followed by a decrease whereas for glutenin both parameters continued to increase in the strain stiffening for glutenin compared to gliadin. Gliadin molecules only display intramolecular disulfide bonds creating a great deal of mobility whereas for glutenin molecules, which contain both intermolecular and intramolecular disulfide bonds, the strong network structure formed by this molecular arrangement results in very pronounced strain stiffening.

Tuesday 14:30 Fredensborg

Assessment of oral processing properties of fermented milk products by tribology measurements <u>Patrizia Buldo</u>, Tina Hoegholm, and Ditte Marie Folkenberg

Fermented Milk & Probiotics, Innovation, Chr. Hansen AS, Hoersholm 2970, Denmark

The bulk texture and the rheological properties of fermented milk products are often not a good indicator of some oral processing properties, such as smoothness and mouth coating. Tribology approaches are increasing due to their ability to better describe the mechanical oral processing properties, when compared to rheological measurements. In the present work, a method to quantify the lubricating properties, such as the friction coefficient, of fermented milk products was design. A broad variety of fermented milk products, differing in composition and in textural properties, were analyzed for their rheological properties with a rheometer. Oral processing and oral textural properties were analyzed with a ball bearing tribometer and with a sensory panel, respectively. Multivariate data analysis was used to find the correlation between the studied variables. The complexity revealed by the oral processing properties measured via friction coefficient indicates a product dependency to the Stribeck curves obtained. The friction coefficients on selected points of the Stribeck curve significantly correlate to some oral evaluated textural properties, such as smoothness, and to the fat content. No significant correlation was obtained between smoothness and the rheological parameters. The present study highlights a novel approach to study oral processing properties of fermented milk products.

Tuesday 14:50 Fredensborg

Development of extruded high-protein alternatives to meat

Mats Stading¹, Marco Berta¹, and Roland Kádár²

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Global meat consumption per capita doubled between 1961 and 2009. Even if the increase in European meat consumption has slowed in recent years, in Europe it is 85 kg per capita, twice the world average, and is forecasted to increase by 10% from 2007 to 2030. In the EU, consumption corresponds to around 20 kg of pure protein; a realistic expectation is that within 10 years this level could be reduced by the introduction of protein-rich vegetable foods and educational programs to 10 kg of animal protein per year. The increases in meat eating are alarming from the nutritional perspective, as excessive consumption has been linked to health problems. Expansion of animal production results in undesirable clearing of forestlands and increases in emissions of climate-affecting gases. It is clear that increased intake of vegetable alternatives is preferable for economical, sustainability, and health reasons. All new alternatives to meat will have to be sufficiently attractive in their own right to make their way into the market. Clearly, if the alternatives do not appeal to us both aesthetically and nutritionally, we will stick to meat beyond what we and the planet can manage.

By combining food science, materials science, rheology and creative culinary ingenuity we have developed healthy, plant-based protein foods with low carbon footprint that are equally attractive to meat. Starting from a mixture of proteins we have extrude structures with fibrous, desirable texture and chewiness. The taste and flavor of this matrix is bland and an experienced chef has applied his magic to create succulent protein food dishes (smat.nu).

The use of plant based protein ensures a "climate smart" product, which is also healthy due to the protein quality of the mixture. The influence of rheology in the extrusion process is crucial for the development of the final structure, which will be demonstrated in the conference contribution.

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Tuesday 15:10 Fredensborg

The effect of Prunus cerasus gum exudates addition on physic-chemical, rheological and sensory properties of yogurt

Sara Khosrowshahi¹ and Mohammad Ali Hesarinejad²

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In this work, the influence of Prunus cerasus gum exudates (PCGE) at various concentrations on rheological, technological, chemical and sensory characteristics of yogurt was evaluated. The use of PCGE in the yogurt significantly decreased the values of pH. The degree of syneresis of the samples decreased from 4.3 to 2.4 (mg/30g) when PCGE concentration elevated from 0 to 4%. Rheological measurement indicated that with increasing PCGE concentration, consistency coefficient values increased which is a typical change of yogurt as a consequence of hydration of molecules and added stabilizers. With the incorporation of PCGE to yogurt formulation, the degree of whiteness decreased. Based on sensory evaluation, addition of PCGE led to improve taste, texture and overall acceptability values of the samples. Yogurt containing 4% PCGE had highest overall acceptability.

Keywords: Prunus cerasus gum exudates; Yogurt; Rheological properties; Physicochemical properties, Sensorial characteristics.

Tuesday 16:00 Fredensborg

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The impact of water content, mixing time and fermentation on the rheological behaviour of wheat flour dough

<u>Mathieu Meerts</u>¹, Ruth Cardinaels², Filip Oosterlinck³, Christophe M. Courtin⁴, and Paula Moldenaers¹ ¹Department of Chemical Engineering, KU Leuven, Leuven 3001, Belgium; ²Department of Mechanical Engineering, TU Eindhoven, Eindhoven 5600 MB, The Netherlands; ³Materials Science Centre, DSM Ahead B.V., Geleen 6167 RD, The Netherlands; ⁴Department of Microbial and Molecular Systems, KU Leuven, Leuven 3001, Belgium

The breadmaking performance of wheat flour dough is largely determined by the gluten network, and is closely related to its rheological properties. Investigating the impact of the main process parameters in the breadmaking protocol (i.e. water content and mixing time) on the rheological behaviour of bread dough is therefore of major interest for the baking industry. In this work, the effects of water content and mixing time on the rheology of unfermented dough have been studied systematically. Thereto, a rheological toolbox consisting of linear and non-linear tests in shear and extension has been used. The effect of water content on the dough behaviour can be captured by simple scaling laws, which were found to be valid not only in the linear region, but to a certain extent also in the non-linear region. At sufficiently high water levels, a `free' water phase exists, which fills the interstitial spaces between the starch granules and gluten proteins. The water thereby attenuates the starch-starch and gluten-starch interactions, which are known to dominate the dough response in the linear region. Overmixing may cause the gluten network to disintegrate, resulting in a substantial attenuation of the strain-hardening behaviour. The adverse effects of overmixing are significantly less pronounced when the mixing action is performed in an oxygen-lean environment. If allowed some rest time, the overmixed dough shows signs of recovery. The recovery is rather slow, however, and depending on the inflicted amount of damage it may not be complete either. Finally, we set out to assess the potential of fundamental rheological techniques to study the rheology of fermented dough. Apart from the carbon dioxide gas, other yeast metabolites such as ethanol and succinic acid also have a significant impact on the rheological behaviour of dough. Both components affect the gluten network, and tailoring their concentration might therefore constitute a promising tool to optimise the dough performance.

Tuesday 16:20 Fredensborg

Gels of carrageenan from different origin, fall on a master curve

Heidi L. Pedersen, Jan Larsen, Jette Andersen, and Iben Hemmingsen

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Milk and water gels prepared with carrageenan as stabilizer were characterized using texture analyser. A texture analyser is an easy to use and widely applied equipment for characterization of gels in the food industry. Typically a probe is penetrated into a gel, that is cast in a container. This set-up allows measuring gels, that are not self supporting or very brittle. Carrageenan from different origin i.e. Spinosum, Cottonii, Chondrus and Gigartina with different molecular weight, carrying different counter ions, were used for preparation of gels . Gel properties in two different standardized systems were determined using texture analyzer - water gels with 1% carrageenan in deionized water, and milk gels with 0.3% carrageenan in a dessert formulation prepared from UHT milk and sugar. Results of break and gel strength revealed that the carrageenan types fall in two groups, one group has a soft and elastic texture, and the other showing a firm and brittle texture. Actually, if forming a gel, the distance to break and gel strength of carrageenan samples fall on a sort of master curve, independent of origin, molecular weight and counter ions. Gels are either firm and brittle or soft and elastic, nothing in between.

Tuesday 16:40 Fredensborg

Effect of cellulose-based hydrocolloids and starch chemical modification on the rheology of gluten-free dough

Marco Berta¹, Ingrid Koelewijn², Kalle Johansson³, and Mats Stading¹

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This study was carried out to evaluate the effect of cellulose-based hydrocolloids on the rheology of flour doughs based on corn starch and potato starch. This type of dough has a shear-thickening behavior if no hydrocolloid is added and it would not proof even at high temperature and relative humidity, being thus unsuitable for bread baking. Adding hydroxypropylmethyl-cellulose (HPMC) in the dough

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imparted a shear-thinning behavior and allowed significant volume increase upon proofing. To understand the effect of the hydrocolloid chemical structure on the dough rheology, HPMC was exchanged with ethyl(hydroxyethyl)cellulose (EHEC). Tuning of the EHEC chemistry either by methylation or by hydrophobic modification greatly affected the dough rheology. An attempt to obtain a result similar to that of HPMC was also made using potato starch modified through methoxyl and hydroxypropyl substitution, instead of adding cellulose-based hydrocolloids. This produced a strong elastic dough but little volume increase upon proofing.

Tuesday 17:00 Fredensborg

Characterization of a model food crystal network oleogel formation an aging

<u>Denis C D Roux</u>¹, E M Spiden², Francois Caton³, N ISOBE⁴, Olivier Schafer⁵, J CRAVEN⁶, and D Z GUNEZ⁷ ¹Laboratoire Rhéologie et Procédés, University Grenoble Alps, Grenoble, France; ²Laboratoire Rhéologie et Procédés, Univ. Grenoble Alpes, Gières, Rhone-Alpes 38610, France; ³Laboratoire Rhéologie et Procédés, University Grenoble Alps, Grenoble, France; ⁴Laboratoire Rhéologie et Procédés, Univ. Grenoble Alpes, Gières, Rhone-Alpes 38610, France; ⁵Nestlé Research Center, Lausanne, Switzerland; ⁶Nestec, Nestlé Research Center, Lausanne, Vaud 2222, Switzerland; ⁷Nestec, Nestlé Research Center, Lausanne, Vaud 2222, Switzerland

Monoglycerides (MG) suspended in oil are very important systems in the cosmetic and food industries. Indeed their mechanical properties, bio-compatibility, weak susceptibility to microbial infection, and excellent emulsification properties make them ideal to tailor cream products for cosmetic and food applications. However, while MG in water systems have been studied in-extenso, MG in oil systems are less well known, in particular the aging of their physical properties. In this work, we investigated the behaviour of an oleogel made from 10% commercial, distilled monoglycerides in sunflower oil. The gel was characterized in terms of crystal micro-structure, rheology, and polymorphic state as it was cooled to 25° C, and as a function of age for up to 8 weeks. As the solution was cooled from 95° C to 25° C, two distinct polymorphic events occurred: crystallization into the initial a phase, and a transition into the sub-a from; both events were correlated with highly birefringent crystals and a large increase of visco-elasticity. Over 8 subsequent weeks the gels evolved from the initial polymorphic forms to the ß polymorph, and the initial percolating crystal network transitioned into discrete, dense crystals, with an associated decrease in gel strength. During both cooling and aging, the polymorphic evolutions and rheological properties is hypothesised to be extendable to other lipid oleogel systems, providing important tools to predict gel properties, including gel collapse, in industrially interesting lipid-based materials.

Tuesday 17:20 Fredensborg

The oral phase of swallowing of Newtonian and non-Newtonian liquids

<u>Marco Ramaioli</u>¹, Saviz Mowlavi², Marco Marconati¹, Adam Burbidge³, Hayoun Pascaline⁴, Benjamin Le Reverend³, and Jan Engmann³

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The anatomy of the upper throat enables complex physiological processes like swallowing, breathing and speaking. Ageing and neurological disorders can however reduce the coordination in tongue peristalsis and alter the transient bolus flow during swallowing, exposing patients to the risk of bolus aspiration and pneumonia, or dehydration and malnutrition. In this study, an in vitro device that mimics the oral phase of swallowing is calibrated using in vivo ultrasound measurements. The oral flow behavior of different Newtonian and non-Newtonian liquids is then investigated in vitro and in vivo, revealing that shear-thinning thickeners used in the treatment of dysphagia behave very similar to low-viscosity Newtonian liquids during active swallowing, but provide better control of the bolus before the swallow is initiated. A theoretical model is used to interpret the experimental results and enables the identification of two dynamical regimes for the flow of the bolus: first, an inertial regime of constant acceleration dependent on the applied force and system inertia, possibly followed by a viscous regime. The effect of the liquid rheology on the total oral transit time is strong when the second regime dominates the bolus flow. This theory provides a plausible explanation for similarities and differences in swallowing performance of shear-thinning and Newtonian liquids. The theory also suggests that while the effects of system inertia are significant in this transient flow, the density of the bolus itself plays a negligible role in its dynamics. This is confirmed by experiments on a high density contrast agent used for videofluoroscopy, revealing that rheologically matched contrast agents and thickener solutions flow very similarly. The approach and the results presented in this study pave the way toward a mechanical model of human swallowing that would facilitate the design of novel, physically sound, dysphagia treatments and their preliminary screening before in vivo evaluations and clinical trials.

Tuesday 17:40 Fredensborg

Tribology and Rheology of potato chips during in vitro oral processing

<u>Omkar S. Deshmukh</u>¹, Sushil Dhital², Stefan K. Baier³, and Jason R. Stokes¹ ¹Chemical Engineering, University of Queensland, St Lucia, Queensland 4072, Australia; ²Centre for Nutrition and Food Sciences, Queensland Alliance for Agriculture and Food Innovation, St Lucia, Queensland 4072, Australia; ³PepsiCo Long term Research, Hawthorne, NY 10532, United States

Oral processing of solid foods is an extremely dynamic and complicated process that involves multiple processes in tandem such as comminution, mixing, dilution, hydration and enzymatic breakdown that gradually transform the food from a morsel or a bite to a bolus that is ready for swallowing. This work aims to develop new methods to determine relevant properties of solid snack foods relevant to the dynamic sensory response. The specific focus here is on capturing the effect of hydration on the tribology and rheology of comminuted potato chips (or crips) (PCs), which are formed from sliced potato (fried PC) or manufactured- from reconstituted potato cells (baked and fried).

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The use of new techniques such as Ring Shear Tester (RST) are investigated to probe the effect of hydration on friction and cohesion between the particles of various types of comminuted chips. In addition, we also study the rheology of hydrated PCs using a vane geometry.

Whilst the major contribution to the bolus rheology comes from the solid content, differences between samples are partially explained by the micromechanics of the bolus, which is probed using Gap Dependent Rheology (GDR). We discover that differences between the Fried and the fabricated chips arise out of their structure and starch properties. These differences also show up in the RST data where at high moisture content, the fabricated PCs showed higher cohesion as compared to the Fried PC.

Symposium SG

Solids, glasses, and composites

Organizers: Jeppe C. Dyre and Esmaeil Narimissa

Tuesday 13:30 Kronborg

Assessment of the degree of dispersion for polymeric nanocomposites via FT-rheology Mingeun Kim and Kyu Hyun

School of Chemical and Biomolecular Engineering, Pusan National University, Busan, Republic of Korea

Owing to high surface area of nanoparticles, polymeric nanocomposites show greater properties than conventional composites. Up to date, numerous researches have focused on enhancing the dispersion quality whereas relatively few researches have been concentrated on assessing that. In order to characterize the morphology of polymeric materials, optical analysis, e.g. TEM, XRD, SAXS and also rheological measurements have been employed predominantly. Among rheological measurements, SAOS (Small Amplitude Oscillatory Shear) test is the well-known test to stand for dispersion state of polymer composites. Storage modulus (G') is the well-known parameter to represent morphological evolution as a result of lower scaling behavior with power(G'??ⁿ) at low frequencies. Yield stress values also symbolize the degree of dispersion for polymer nanocomposites. However, SAOS results are not enough to express the morphological states quantitatively. Recently, Lim et al.^[1] suggested new parameter, NLR (Non-linear Linear viscoelastic Ratio) originated from FT (Fourier Transform)-rheology under LAOS (Large Amplitude Oscillatory Shear) flow, that implies the degree of dispersion for polymer nanocomposites altered by the compatibilizer and hydrophobicity, for example, polypropylene/clay with maleic anhydride grafted polypropylene and polypropylene or polyethylene oxide with various nano-silica particles. SAOS and LAOS results exhibit similar leaning on the samples with aid of the compatibilizer. Interestingly, those by hydrophilicity show different tendency. In combination with TEM images, it is obvious for polymer nanocomposites that LAOS results imply the dispersion state more than those of SAOS.

[1] Lim et al., 2013, Nonlinear viscoelasticity of polymer nanocomposites under large amplitude oscillatory shear flow, J. Rheol. 57, 767-789.

Tuesday 13:50 Kronborg

Structural reorganization of CNC in injection-moulded CNC/PBAT nanocomposites under thermal annealing

Nadia El Kissi¹, Marcos Mariano², and Alain Dufresne³

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Nanocomposites were prepared by extrusion and injection-moulding from polybutyrate adipate terephthalate (PBAT) and high aspect ratio cellulose nanocrystals (CNCs) extracted from capim dourado fibres. Three CNC contents were used corresponding to 0.5, 1 and 2 times the theoretical percolation threshold. Small amplitude oscillary shear (SAOS) experiments show that as the CNC content increases, a more elastic behaviour is observed but no percolating network can form within the polymeric matrix due to the high shear rates involved during the injection-moulding process. Annealing of the samples at 170°C was performed and the possible reorganization of the nanofiller was investigated. This reorganization was further elucidated using 2D-SAOS and creep experiments.

Tuesday 14:10 Kronborg

SG8

Thermo-rheological behavior of thermoplastics polyurethanes and graphene oxide based nanocomposite

<u>Ricardo E. Andrade</u>¹, Leice G. Amurin¹, Pablo R. Muñoz¹, Camila P. Oliveira¹, Guilhermino M. Fechine¹, Chaitanya Danda², and Joao Maia²

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Thermoplastics polyurethanes are materials with many interesting properties and structures. Their peculiar properties are due to microphase-separated morphologies, which develop according to immiscibility between hard urethane containing segments and soft segments. The graphene oxide (GO) has been studied in the context of many applications, such as polymeric nanocomposites. These particles 2D are able to tailor the excellent electrical, mechanical, and thermal properties of the thermoplastic polyurethane. When graphene oxide is added to the thermoplastics polyurethanes, different interactions between each domain and 2D particles resulting in complex structure. These complex structures will give a different footprint on the rheological behavior to the thermoplastic polyurethane graphene oxide based nanocomposites. In this work, the phase transition behavior of thermoplastic polyurethane is investigated by rheological tests. Rheological measurements display a phase transition at range temperature. Oscillatory shear flow measurements are performed to

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investigate relationship between structure and viscoelastic properties of thermoplastic polyurethanes, in particular, the influence on the phase transition of the polymeric matrix when 2D particles (GO) are dispersed.

Tuesday 14:30 Kronborg

Rheological properties of PEG/CNC nanocomposites prepared by solution mixing: effect of ultrasonication method

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The rheological properties of suspensions of cellulose nanocrystals (CNCs) in molten polyethylene glycol (PEG) were investigated. The CNCs were obtained from sulfuric acid hydrolysis of wood pulp and were supplied by FPInnovations, both before and after a spray or freeze drying process. Ultrasonication was used to improve the CNC dispersion in deionized water, after which the suspensions were mixed with an aqueous PEG solution at room temperature. The samples were subsequently dried at 50°C under vacuum for 48 h and compression molded at 80°C for 10 min. In the molten state, the PEG/CNC nanocomposites exhibited a yield behavior and percolation at a low volume fraction of 0.04%. The elastic modulus is higher than the loss modulus and both were almost independent of frequency. These results were characteristics of a percolation network and suggested both a very good dispersion of CNC in PEG and a screening of OSO3- charges on the surface of the CNCs. Moreover, the gel-like behavior of the PEG/CNC nanocomposites was the same, whatever the method of dispersion of the CNCs in water by ultrasonication. The yield stress increased as a function of volume fraction to the power 1.8 for all systems studied and the CNC percolation network exhibited a floc structure characterized by a fractal dimension close to 2, in agreement with literature results. This work showed the important potential of CNCs to reinforce thermoplastics.

Tuesday 14:50 Kronborg

SG10

SG11

Multiscale modelling approach to the rheological behaviour of polymer nanocomposites: Nonequilibrium thermodynamics modelling coupled with NEMD simulations

Pavlos S. Stephanou¹, Dimitrios G. Tsalikis², Panagiotis V. Alatas², and Vlasis G. Mavrantzas³

¹Department of Mathematics and Statistics, University of Cyprus, Nicosia, Cyprus; ²Department of Chemical Engineering, University of Patras, Patras, Greece; ³Department of Mechanical and Process Engineering, ETH Zurich, Zurich, Switzerland

Polymer matrix nanocomposites (PNCs) are formed by adding nanoparticles (NPs) to a polymer matrix. In the present work we proposed a multiscale approach to study the rheology of PNCs with spherical inclusions by interfacing rheological models with non-equilibrium molecular dynamic simulations (NEMD). At the heart of our work is a mesoscopic rheological model for PNCs derived in the framework of the Generalized Bracket formalism of nonequilibrium thermodynamics [P.S. Stephanou, V.G. Mavrantzas, G.C. Georgiou, Macromolecules 2014, 47, 4493-4513]. The model was initially developed for unentangled PNCs and showed a very promising comparison with experimental data regarding the phase behaviour, conformational properties and rheological properties of these materials. In the absence of chain elasticity, the new model reduces to the Jeffery constitutive equation for the rheology of a Newtonian suspension of spheroidal NPs. The model addresses NPs of spherical shape by constraining the orientation tensor to be always equal to its equilibrium value, and provides predictions for the phase behaviour and rheological properties in shear that are consistent with experimental data. In a second step, atomistic NEMD simulations are carried out with model PNCs systems similar to those used in experimental studies in order to get estimates of the values of the parameters appearing in the mesoscopic model. Key among these parameters is the polymer chain relaxation time and its dependence on the volume fraction of NPs. Additional parameters refer to the degree of interaction between polymer chains and NPs or between NPs and NPs. Our combined theoretical-simulation work provides a unified approach to the phase behaviour, chain conformation, swelling and rheological properties of PNCs melt, as a function of NP volume fraction, NP size, and imposed deformation rate.

Tuesday 15:10 Kronborg

Novel rheological analysis approach for assessment of dispersion grade in polyethylene-clay-ZnO nanocomposites

Milan Kracalik

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Polymer-clay nanocomposites exhibit complex rheological behaviour due to physical and possibly also chemical interactions between individual components (polymer, clay, compatibilizer in case of unpolar polymer), which can be detected by rheology. Usually, flow behaviour of multiphase polymer systems has been described by storage flow part through the viscosity curve (shear thinning phenomenon) or storage modulus curve (formation of secondary plateau) and by loss flow part through dumping behaviour (e.g. Van Gurp-Palmen-plot, Cole-Cole plot), respectively.

On the contrary to typical rheological analysis, new approach using information about storage flow part has been introduced for description of physical network made of rigid particles in polymer matrix as relation of $\int G'/\int G''$ over specific frequency range. This approach has been experimentally proved for polymer nanocomposites in order to evaluate both shear as well as elongational flow field. In this contribution, polyethylene-clay-ZnO nanocomposites with different dispersion grades have been prepared and changes in physical network have been analysed by novel "melt rigidity" approach using different cumulative rheological parameters. It has been found that information obtained from specific cumulative rheological parameters allows clear comparison even of small differencies in physical network of nanocomposites. This new approach was in good accordance with information gained from conventional evaluation approach like shear-thinning or G' secondary plateau analysis.

Tuesday 16:00 Kronborg

Broadband rheological techniques covering seven decades from 1 mHz to 10 kHz

Tina Hecksher, Mikkel H. Jensen, Henriette W. Hansen, Bo Jakobsen, Kristine Niss, and Tage E. Christensen

IMFUFA, DSE, Roskilde University, Roskilde 4000, Denmark

This paper presents two techniques developed for measuring the complex shear modulus respectively bulk modulus of supercooled molecular liquids and glasses of an unmatched broad range of frequencies. The techniques relies the piezo-electric properties of certain ceramic materials to shear or compress the sample while monitoring the resulting capacitance of the piezo-electric ceramic material. The devices are small compared to conventional rheometers and thus their internal mechanical resonances are pushed towards higher frequencies. The techniques are optimized for moduli from about 1 MPa to 10 GPa. By combing the two methods we can determine the viscosity over 11 decades from 10 Pas to 10^12 Pas. In the paper we give a flavor for the a variety of research contexts where the techniques have played a crucial role. These include: testing of theories for the glass transition [e.g., Gundermann et al Nat. Phys. 7, 816 (2011), Jakobsen et al J. Chem. Phys. 136, 081102 (2012)], testing models connecting electrical and mechanical properties of supercooled liquids [e.g., Niss et al J. Chem. Phys., 123, 234510 (2005), Gainaru et al J. Chem. Phys. 137, 064508 (2012)], investigating the polymer-like structures in hydrogen-bonded systems [e.g., Gainaru et al Phys. Rev. Lett. 112, 098301 (2014), Jakobsen & Hecksher J. Chem. Phys., 144, 161103 (2016)], and the general characterization of mechanical properties of liquids [e.g., Maggi et al J. Phys. Chem. B 112, 16320 (2008), Hecksher et al J. Chem. Phys. 138, 12A543 (2013), Gundermann et al J. Chem. Phys. 140, 244508 (2014)]. In addition, we present some recent adaptations of the shear rheological device enabling us to measure shear properties of rubber and bitumen.

Tuesday 16:20 Kronborg

Impact of structural order on shear thinning in supercooled, glass-forming liquids

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Nonlinear rheological response, e.g., the change of viscosity as a function of shear rate, has attracted considerable attention over the years from both fundamental and applicational viewpoints. Strong nonlinear rheological response is observed near the glass transition where dramatic dynamical slowing down also takes place. The basic mechanism behind this nonlinearity, however, still remains unclear. As an example, even the fundamental question of what is the system's internal relaxation rate which competes with the shear rate has not yet been answered. In this study, we address this question by molecular dynamics computer simulations of size polydisperse particles under simple shear. We reveal that the timescale associated with onset of shear thinning is determined by the characteristic lifetime of structural order fluctuations. A supercooled liquid starts to feel and remember shear-induced anisotropy as the shear rate exceeds this new characteristic timescale and happens much earlier than the structural relaxation rate of the liquid. Our findings emphasize the importance of static structural order in understanding sheared supercooled, glass-forming liquids.

Tuesday 16:40 Kronborg

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Development of smart mold flux showing dual viscous functions for good lubrication and prevention of slag entrainment in a continuous steel caster mold

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Optimization of CaO-SiO2-CaF2 based flux in a continuous steel caster should be determined from the view point of dual viscous functions for minimizing slab surface defects - high viscosity enough to alleviate flux entrainment at mold top surface where shear rate is about 10 - 40 reciprocal second and low viscosity enough to maximize lubrication capability at oscillated mold wall region where shear rate is around 100 - 1000 reciprocal second. Appropriate liquid mold flux with a strong shear thinning behavior showing significant decreasing tendency of viscosity with increasing shear rates has to be developed for sound slab quality. Flux viscosity was measured by a rotational type viscometer as a function of shear rates. Raman and XPS analysis were employed to understand structural changes of flux for correlating with shear thinning behavior. The present work has focused on developing an optimum mold flux system with strong shear thinning behavior appropriate for dual viscous functions could be achieved by incorporating silicon nitride or silicon carbide into network structure of the liquid flux. The flux compositions with a strong shear thinning behavior will be presented from the viewpoint of clean slab production.

Tuesday 17:00 Kronborg

From simple to complex glass-forming liquids: broadening of the glass transition as studied by shear rheology

Olli-Ville Laukkanen¹, H. Henning Winter², Hilde Soenen³, and Jukka Seppälä⁴

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In the current literature, there seems to be a complete lack of research on the rheological properties of complex glass-forming liquids, i.e. molecular glass-forming liquids that are comprised of a variety of different molecules and exhibit many types of intermolecular interactions. This study focuses on the rheological characterization of complex glass-forming liquids (CGFL) in shear and compares their rheological behavior with that of simple glass-forming liquids (SGFL). Various petroleum liquids are used as model materials for CGFLs and their low-temperature rheological properties are measured by small-diameter parallel plate rheometry. Rheological data for three

SGFLs are obtained from Hutcheson and McKenna [1]. A comparison of the viscoelastic data of SGFLs and CGFLs in the Booij-Palmen plot $\delta(\log|G^*|)$ reveals a broadening of the glass transition related dynamics in CGFLs. Furthermore, this broadening effect is clearly visible in the shape of the calculated relaxation time spectra; the linear viscoelasticity of SGFLs is described by a power-law spectrum with a sudden cutoff at the longest relaxation time [2], whereas the power-law spectrum of CGFLs has a broad cutoff. The relaxation time spectra of CGFLs are fitted with the broadened power-law spectrum (BPLS) model [3], and the stretching exponent β is used to describe the broadness of the BPLS spectrum at long relaxation times. β is observed to decrease systematically with the increasing complexity of a glass-forming liquid. Finally, it is shown that β correlates with the width of the glass transition region as measured by differential scanning calorimetry (DSC), providing a connection between the dynamic and thermodynamic measures of the broadness of the glass transition.

[1] S.A. Hutcheson & G.B. McKenna, J. Chem. Phys., 129, 074502 (2008) [2] H.H. Winter, Macromolecules, 46, 2425 (2013) [3] O.V. Laukkanen, H.H. Winter, H. Soenen & J. Seppälä, Annu. Trans. Nord. Rheol. Soc., 24, 17-21 (2016)

Tuesday 17:20 Kronborg

Crystal Growth in Fluid Flow: The Role of Nonlinear Rheology

Hailong Peng, Dieter M. Herlach, and Thomas Voigtmann

Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt, Köln, Germany

We study crystal growth kinetics in a supercooled fluid in the presence of strong shear flow, by using molecular-dynamics computer simulations. Close to the equilibrium melting point, shear flow always suppresses the growth velocity of the crystal-liquid interface. For lower temperatures, however, we find that the growth velocity depends non-monotonically on the shear rate. Slow enough flow enhances crystal growth; stronger flow gives rise to a regime where the growth velocity decreases with increasing shear rate and is nearly temperature-independent, in striking contrast to what one expects from thermodynamic and equilibrium kinetic properties of the system. We rationalize these results as the effect of the nonlinear rheology of the sheared fluid: while initially, shear thinning causes an enhanced particle mobility and thus aids the transport of particles to the interface, eventually the supercooled fluid approaches yield-stress flow behavior and sets a temperature-independent but strongly shear-rate dependent kinetic limit to crystal growth.

Symposium GS

Gels and self-assembled systems

Organizers: Moshe Gottlieb and Henning H. Winter

Tuesday 13:30 Schackenborg Adaptive microgels in bulk and at interfaces Walter Richtering

Walter, RWTH Aachen, Aachen, Germany

We investigate the influence of the structure of microgels on their behavior at interfaces. In particular we study three different types of microgels: (i) core-shell microgels with a solid silica core surrounded by a cross-linked poly(N-isopropylacrylamide) polymer shell (with different cross-link densities); (ii) the corresponding hollow microgels where the core was dissolved; and (iii) ultra-low cross-linked PNIPAM microgels. The structure in solution was determined by means of neutron and light scattering. The structure of the microgels at interfaces was investigated by scanning force and electron microscopy. Compression isotherms of the microgel-laden oil-water interfaces were determined. They show that the removal of the core leads to an increase of the surface pressure at low compression and the same effect can be observed when the polymer crosslink density is decreased. Low cross-link density and a missing core thus facilitate spreading of the polymer chains at the interface and, at high compression, hinder the transition to close hexagonal packing. It is especially remarkable that a low cross-link density leads to a high compression modulus at low compression, while this behavior is reversed at high compression. This is related to an enhanced spreading of polymer chains at the interface and thus high adsorption energy. These conclusions are fully supported by computer simulations, which show that the cross-link density of the polymer shell defines the degree of deformation at the interface. Additionally, the core restricts the spreading of polymer chains at the interface. These results illustrate the special behavior of soft microgels at liquid interfaces.

Tuesday 14:10 Schackenborg

Metallo-supramolecular hydrogels under superposition flows

Jan Hendricks¹, Jérémy Brassinne², James D. Wilson³, and Christian Clasen¹ ¹Department of Chemical Engineering, KU Leuven, Leuven, Belgium; ²Research and Innovation Centre Lyon, Solvay, Saint-Fons 69190, France; ³Research and Innovation Centre Paris, Solvay Novecare, Aubervilliers Cedex 93308, France

The behavior of associative polymers under shear receives currently a lot of attention. Depending on the utilized association mechanism, e.g. hydrophobic interactions, hydrogen bonding or complexation, and the physical as well as chemical properties of the polymers, a range of complex material responses have been observed when the polymers are exposed to shear flow. Besides shear thickening and shear thinning, also strain hardening and strain softening have been observed. In the current study we investigate hydrogels comprised of a polymeric backbone with ligands distributed along the chain. The addition of different metal ions leads to supramolecular assemblies that form hydrogels when dissolved in water. The hydrogels properties are highly tunable by altering the ratio of metal ions to ligands, the polymer concentration, the density of ligands along the backbone or the metal ion species. An open question is the mechanistic origin of the observed shear thickening as well as shear thinning. This behavior is believed to be related to the conformation of the polymer coils under flow and therefore to a flow dependent network volume. This might lead to an alteration of the amount of intermolecular bonds and thus a

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strong rate dependency, which are broken when the shear rate is further increased. To explain into the mechanisms leading to these nonlinear shear induced effects, orthogonal superposition measurements that were performed by superimposing small amplitude oscillatory shear parallel and orthogonal to steady shear flow. Using frequency as well as time dependent data collected in both directions we demonstrate how the anisotropy of the hydrogel network structure and morphology is affected by the flow behavior, in order to elucidate the observed macroscopic flow properties.

14:30 Schackenborg Tuesday

Associative polymers based on reversible covalent chemistry: microscopic modeling and flow behavior

Michel Cloitre¹, Rémi Fournier¹, and Stéphane Jouenne² Soft Matter and Chemistry, ESPCI Paris, PSL Research University, CNRS, Paris 75005, France; ²Pôle d'Etudes et de Recherches de Lacq, Total SA, Lacq 64170, France

We present a novel concept of water soluble associative polymers based on reversible covalent chemistry. Partially hydrolyzed poly(acrylamide) grafted with boronic acid moieties interact with poly(vinyl alcohol) chains through a molecular recognition mechanism. Mixtures exhibit remarkable viscoelastic properties which can be tuned at will through the polymer concentration, grafting density, ionic force, temperature, and pH. Viscous solutions with significantly enhanced viscosity are formed at low concentration and viscoelastic gels at higher concentrations. The crossover concentration between the two regimes is very low making this system promising for applications.

Viscoelastic gels exhibit Newtonian behavior at low shear rates, shear-thickening, and shear-thinning regime at higher rates. We will present a microscopic model which connects the relaxation time to the strength of the covalent associations between boronic acids and diols, which are ultimately controlled by the pH. Weak gels formed at neutral pH flow like ordinary viscoelastic solutions but strong gels exhibit a variety of flow heterogeneities like wall slip and unstable shear banding, depending on the boundary conditions. Our results demonstrate the link between a particular flow scenario and the strength of associations.

Tuesday 14:50 Schackenborg

How does gelation stabilize aqueous foams?

Sylvie Cohen-Addad¹, Houda Bey², and Olivier Ronsin³

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Liquid foams are unstable due to aging processes such as drainage, coalescence or coarsening (1). Since these processes modify their structure, they can be a severe limitation in the elaboration of solid foams with controlled structures inherited from their liquid precursors (2, 3). Here we study how coarsening can be inhibited either by a mixture of gas containing a species insoluble in the foaming solution, or by gelation of the foaming solution, or by both effects. Soft hydrogel foams are of interest for medical applications that require biocompatibility or in green chemical engineering. We present experiments with monodisperse ordered liquid foams, produced using a microfluidic device fed with a hydrogel solution above its gelation temperature. A gas mixture with a controlled partial pressure of an insoluble gas is used to inflate bubbles. As the foam is quenched below the gelation point, the shear modulus of the gels starts to build up. Our experiments show that even though gelled foams are soft solids, they can be either stable or unstable, depending on the competition between Laplace pressure, elastic stresses in the gel and the osmotic pressure due to the insoluble species. We identify the domain of foam stability depending on the bubble radius, the number of trapped species molecules in a bubble, and the gel shear modulus. We derive a mean field model that takes into account the combined effects of an insoluble gaseous species and the gel elastic stresses in a gelled foam on coarsening. The domain of stable foams is governed by a characteristic elasto-capillary radius set by the ratio of surface tension to storage modulus. The predicted 3D diagram of foam stability is in qualitative agreement with our data.

(1) Cantat, Cohen-Addad et al, Foams: Structure and Dynamics, OUP (2013)

(2) Scheffer, Colombo, Cellular Ceramics: Structure, Manufacturing, Properties and Applications, Wiley (2005)

(3) Testouri, et al, Col. Surf. A, 413, 17-24 (2012)

15:10 Schackenborg Tuesday Yield Strain of a Physical Gel with Memory

Vijesh A. Tanna¹ and H. Henning Winter²

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Yielding was studied with a soft solid, which permanently reduces its internal connectivity under strain and in this way "memorizes" strain events. Oscillatory shear at large stress/strain amplitudes (LAOS) result in an irreversible solid to solid transition. The flow-induced change increases when increasing the imposed strain and prolonging its duration. About the same strain values were found for the onset of nonlinearity in a traditional SAOS to LAOS (StL) stress growth experiment and for yielding in a SAOS-LAOS-SAOS (SLS) experiment. The onset of non-linearity and yielding seems to be strain controlled since the characteristic strain amplitude is independent of frequency and temperature. Not so for the characteristic stress amplitude. Yielding allows flow and naturally introduces a time dependence, which, for instance, becomes apparent in StL when increasing the stress amplitude more slowly (using higher sampling density) and in SLS when increasing the LAOS time. When the stress/strain amplitude in StL is raised too quickly, the linear viscoelastic region appears to be larger than it actually is. The finite rate of yielding must be accounted for in experimental planning. The characteristics of yielding of a physical gel differ greatly from those of the previously shown (Rheologica Acta 29:423-432, 1990) strain-induced bond breaking in chemical gels.

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Tuesday 16:00 Schackenborg

Nonlinear viscoelasticity and generalized failure criterion for polymer gels

Bavand Keshavarz¹, Thibaut Divoux², Sébastien Manneville³, and Gareth H. McKinley¹

¹Department of Mechanical Engineering, Massachussetts Institute of Technology, Cambridge, MA, United States; ²Centre de Recherche Paul Pascal, CNRS, Pessac, Gironde 33600, France; ³Physics Laboratory, Ecole Normale Superieure de Lyon, Lyon F 69007, France

Many biopolymer gels behave as soft viscoelastic solids and exhibit a generic nonlinear mechanical response characterized by pronounced stiffening prior to irreversible failure, most often through macroscopic fractures. Here, we aim to capture these dynamics for a family of prototypical protein gels using a nonlinear integral constitutive equation built upon; (i) the linear viscoelastic response of the network, (which are well described by a fractional model), and (ii) the nonlinear viscoelastic properties of the gel, which are encoded into a nonmonotonic damping function. This formalism quantitatively predicts the strain and rate-dependence of the mechanical response of the hydrogel to a shear start-up experiment, up to the onset of macroscopic failure. The failure of the gel involves irreversible growth of macroscopic cracks. We couple the measured stress response with Bailey's durability criterion for brittle solids in order to predict the critical values of the stress σ_c and strain γ_c at the failure point, and how they scale with the applied shear rate. The excellent agreement between theory and experiments strongly suggests that the crack growth in this soft viscoelastic gel is a Markovian process, and that Bailey's criterion extends well beyond hard materials such as metals, glasses, or minerals.

Schackenborg Tuesday 16:20

Dynamics of interpenetrated networks of entangled associative polymers

Hadi Goldansaz¹, Ashwinkumar Sharma¹, Guilhem Baeza², Michael Wübbenhorst³, and Evelyne Van Ruymbeke¹ ¹Université catholique de Louvain, Louvain-la-Neuve, Belgium; ²Foundation for Research and Technology Hellas -FO.R.T.H, Heraklion, Greece; ³KU Leuven, Leuven, Belgium

Viscoelastic, thermal and mechanical properties of associative polymers have been extensively studied to underline generalities and distinctions of network formation in regard to their architecture, sticker density and association strength. However little work is conducted on mixtures of associative polymers where two dissimilar components, each capable of forming a transient network, are interpenetrated. Viscoelastic properties of such interpenetrated networks are dominated by relaxation of the neat associative polymers, which in turn depends upon the interplay among i) stimuli-responsive dynamics of supramolecular groups, ii) orientational motion of the macromolecular chains as well as iii) possible synergistic effects of the two components. In this work we use well defined segmented and tri-block copolymers to investigate the effect of chain architecture and sticker density on dynamics of interpenetrated networks made up of binary mixtures. The copolymers consist of monodisperse hydrogen bonding hard blocks and entangled flexible soft block(s). The hard blocks associate via transient interactions and crystallize into large groups which act as physical cross-link and form a network. Using rheology and broadband dielectric spectroscopy, dynamics of such interpenetrated networks are investigated all the way from glassy plateau to terminal flow regime. It is evident that at low temperatures, the interpenetrated networks do not possess extra level of heterogeneity as compared to the neat copolymers. As a result, the rubbery plateau modulus scales with the average sticker density as suggested by rubber elasticity theory. On the contrary, the magnitude of the second plateau in storage modulus and the transition to the terminal viscoelastic regime are dominated by the copolymer chains with greater density of hard block, as they possess the highest concentration of tie strands and therefore, the longest relaxation time.

Tuesday 16:40 Schackenborg

Viscoelastic properties and molecular dynamics of transient polymer networks trapped in ideal permanent networks

Tadashi Inoue¹, Takuya KATASHIMA², Kana YAMAZAKI³, and Takamasa SAKAI⁴ ¹Osaka University, Toyonaka, Osaka, Japan; ²Osaka University, Toyonaka, Japan; ³Osaka University, Toyonaka, Japan; ⁴*The Univeristy of Tokyo, Tokyo, Japan*

Viscoelastic measurements were performed on interpenetrating networks, INPs, composed of a uniform permanent network based on 4armed PEG (poly(ethylene glycol)) and a transient network of HUER having associating chain end-groups, to elucidate dynamics of associative polymers trapped in chemically crosslinked polymer networks. Complex moduli of neat HUER aqueous solutions (0.5 ~ 2 wt%) showed nearly a single Maxwellian relaxation. On the contrary, neat permanent networks of tetra-PEG showed ideal elasticity. HUER in tetra-PEG gels showed a single Maxwellian relaxation, but its relaxation intensity was significantly enhanced and the relaxation time was retarded more than 10 times. Molecular dynamics of HUER chains trapped in permanent networks is discussed in terms of entanglements and translational diffusion of associating points.

Tuesday 17:00 Schackenborg

Dissolution of a surfactant paste: a rheometrical study Rossana Pasquino¹, Nino Grizzuti¹, Gu Chong², and Vincenzo Guida²

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The dissolution process of polymers is an important phenomenon in a wide range of applications and it consists of three main steps: the solvent diffusion in the polymer, the polymer diffusion in a liquid layer close to the interface between the polymer and the solvent and the motion of the polymer-liquid interface. The dissolution of surfactant pastes presents some similarities with the polymer dissolution but is made more difficult by the following aspects: 1) surfactant monomers form aggregates of variable size and shape that can vary with dilution and can dynamically form and disintegrate 2) the surfactant paste already contains the solvent (i.e. water), which makes the diffusion

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process "reversible" and more complicated 3) the diffusion coefficient can be dependent in a non-monotonic way on the surfactant concentration, giving rise to multiple interfaces, difficult to be predicted. In view of the above, we performed a rheometrical study on a surfactant paste, based on Sodium Laureth Sulfate (SLES) at 70% w in water, which is widely used commercially. The rheology was measured under two different conditions. Under equilibrium conditions, we were able to build a rheological phase diagram of the system by diluting the paste in order to obtain surfactant concentrations in the range 15-70% wt. We studied linear and non-linear rheology of the solutions at different surfactant concentration, both in steady and in dynamic conditions. We discovered that the SLES surfactant molecule shows a complex behavior in water with a maximum in viscosity positioned at around 50% wt. Under dynamic, transient conditions, the dissolution process was studied via a home-made plate-plate rheometrical device, consisting of a water bath surrounding the surfactant paste, mounted on a classical stress-controlled rheometer (Physica, Anton Paar MCR702). The torque over time during the dissolution process was measured and related to the morphological transitions at the equilibrium conditions.

Tuesday 17:20 Schackenborg

GS16

Relating the expansion of liquid sheets of supramolecular living polymers to their nonlinear rheology

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Organo-gelator are known to self-assemble because of their ability to form intermolecular hydrogen-bonds. The resulting assemblies can be viewed as "living polymers" which undergo scission and recombination mechanisms which affect the overall dynamics of the system. One particularly polymer system is a so-made reversible polymer based on a bis-urea moiety, EHUT, in Dodecane, an apolar solvent. Whereas, its linear viscoelasticity has been investigated thoroughly, little is known about its nonlinear rheological properties. We have studied the nonlinear rheology of this systems at different concentrations and focused on stress relaxation upon cessation of steady flow was conducted to get insights into the characteristic timescales present in the system. Two relaxation processes were observed, a slow time which is comparable to the terminal relaxation time extracted from the linear data and a fast process which was attributed to the breakage and reformation of H-bonds and found to become faster with shear rate. Here, we present a set of impact droplet experiments by hitting a solid target with an EHUT drop and examining the expansion of the freely expanding sheet. We present the phenomenological understanding based on results with droplets from EHUT at different concentrations and different impact velocities in terms of dynamics and stability. Moreover, we attempt at correlating the results with the nonlinear rheology. We find that, ddespite the very high Deborah numbers (based on the terminal relaxation time), no fractures or instabilities were observed. However, at relatively high concentrations fractures and instabilities were observed independently of the terminal relaxation time. The fast nonlinear relaxation time appears to set the scale for fracture. Finally, an effort to understand potential universalities by comparing with impact droplet results from the literature on Newtonian and weakly viscoelastic systems is presented.

Tuesday 17:40 Schackenborg

Dynamics of entangled bulk polymers with metal-ligand interactions

<u>Flanco Zhuge</u>, Jérémy Brassinne, Charles-André Fustin, Jean-François Gohy, and Evelyne Van Ruymbeke Institute of Condensed Matter and Nanosciences, BSMA, Université catholique de Louvain, Louvain-la-Neuve B-1348, Belgium

The advent of supramolecular chemistry in the last decades has provided powerful tools to form "smart" materials with the ability of molecules to self-assemble. They rely on intelligent macromolecules or (supra-)molecular motifs to adapt their structure and properties towards external triggers.¹ However most of these self-assembled materials are studied in solution because commonly used polymers have a glass transition above the room temperature. But if the material is a fluid itself, i.e. flexible polymers with a glass transition below the ambient temperature, they can be investigated in bulk as soft materials.² Reversible polymeric networks obtained by functionalizing flexible polymer chains with associating units constitutes an interesting and useful class of soft material because of the richness in their rheological behavior such as stimuli-responsiveness, adaptability or healing feature.³

Here, we study the linear viscoelastic properties of a series of low dispersity poly (n-butyl acrylate) chains functionalized with 2,2';6',2"-terpyridine, able to self-associate through metal-ligand coordination. Depending on the topology and functionality of the chains, the polymers with low dispersity ($\theta < 1.3$) self-assemble into metallo-supramolecular bulk structures once metal ions are added. Upon self-assembly, linear building blocks form longer entangled chains while four-arm stars can form entangled networks. The properties of the obtained materials can be finely tuned depending on the length of the polymer chains and the type of metal. In this respect, a control is gained over the dynamics of this class of metallo-supramolecular assemblies. Hence, they are extremely interesting for specific applications such as adhesives or mechano-sensors.

References

1.Gels 2015, 1, 235-255. Macromolecules 2014, 47, 4514-4524. 2.Macromolecules 2015, 48, 7320-7326. Polymer 2015, 69, 233. 3.J. Chem. Soc. Rev. 2012, 41, 909-930. Macromolecules 2014, 47, 2122-2130.

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Wednesday Morning

Symposium PL

Plenary Lectures

Wednesday 8:30 Grand Ball Complex

PL2

Soft matter rheology, tribology and biointerface science: from food structure design to plant cell walls Jason R. Stokes

Chemical Engineering, University of Queensland, St Lucia, Queensland 4072, Australia

Multi-scale rheology, soft-tribology, and soft matter physics as well as colloid, surface and biointerface sciences are playing an integral part in the development of measurement capabilities and knowledge for enabling rational food structure design, as well as more generally for defining micromechanical models in soft systems such as plant cell walls.

This presentation considers new approaches to improve quantification of relevant structure-property-processing (SPP) relationships of soft food materials for situations spanning manufacturing processes to oral processing and digestion. This includes highlighting recent progress and new multiscale techniques in rheology and tribology for quantifying how oral processing transforms food during consumption, where the aim is to determine the physical basis for texture and mouthfeel in various multicomponent foods (beverages, semi-fluids/soft solids, solid snacks). A key challenge has been to capture the highly complex interactions that occur with saliva and surfaces. The combination of studies conducted using both model and real food systems are providing superior ability to evaluate new tribological/rheological-based techniques and develop causal SPP relationships. Well-characterised polysaccharides and densely packed microgel suspensions are proving reasonable models for liquid and soft foods, and recent studies indicate an important role of micromechanical and interfacial properties of individual dietary components and whole food systems. The outcomes are being used for the design of next generation foods and beverages that are both nutritionally beneficial and acceptable to consumers.

The presentation also considers the development of new techniques in multiscale rheology, nanoindentation and tribology to study the mechanics of plant cells, microgels, and poroelastic (biphasic) nanocellulose composites, and will highlight how these are informing the development of a new mechanical model of the plant cell wall.

Symposium SC

Suspensions and colloids

Organizers: Norbert Willenbacher and Philippe Coussot

Wednesday 10:00 Grand Ball

Viscosity amplification in dilute suspensions of non-spherical particles in a Carreau matrix fluid

Jan Domurath¹, Marina Saphiannikova¹, Gilles Ausias², Julien Férec², and Gert Heinrich¹

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When non-spherical particles, like rods or discs, are added to a liquid, the increase in viscosity of the mixture is often described by the Lipscomb model. One important result of Lipscomb's model is the prediction of a strong increase in the viscosity of the suspension with increasing aspect ratio of the filler particles. Despite the fact that this model was originally proposed for a Newtonian matrix fluid it is also applied to polymer melts filled with non-spherical particles. Such an approach completely decouples the influence of the particle shape from the non-linear properties of the suspending fluid. Yet, since polymer melts often exhibit strong non-Newtonian behaviour, e.g. shear thinning, it is to be expected that such a superposition will give a wrong prediction of the suspension viscosity.

To investigate this problem we performed a numerical study of a suspension consisting of a non-Newtonian matrix fluid and rigid spheroidal particles. In particular, we simulated different flows of a Carreau fluid around spheroidal particles with different orientations and used numerical homogenization to obtain the intrinsic viscosity of the suspension as function of applied rate of deformation, thinning exponent and aspect ratio. From the results we are able to extract the rheological coefficients A, B and C of the Lipscomb model. In the Newtonian regime simulation results coincide with Lipscomb's predictions for the rheological coefficients. In the non-linear regime of the Carreau model, i.e. at high deformation rates, we found that the rheological coefficients also strongly depend on the thinning exponent. Furthermore, simulation results indicate that the rheological coefficients additionally depend on the particle orientation in the non-linear regime.

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Wednesday 10:20 Grand Ball Some key physical ingredients in dense suspension simulations

Stany Gallier¹, François Peters², Laurent Lobry², and Elisabeth Lemaire²

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This numerical work intends to highlight the most prominent physical ingredients needed for reliable simulations of dense suspensions. We especially address the role of friction, roughness, and long-range hydrodynamics. Simulations show that friction between particles significantly alters viscosity and normal stresses and leads to an improved correlation with available experiments. A new finding is that friction also increases particle diffusion by a factor of two and provides better agreement on the irreversibility threshold in Pine's experiments. Particle roughness is numerically shown to alter rheology only slightly : a large roughness leads to a small decrease in the viscosity since lubrication dissipation is lowered. Frictional roughness seems to minimize this even more and, by and large, roughness size has only limited effects on rheology. However, large roughness and confinement can trigger the onset of particle layering which strongly decreases diffusion. Finally, we have evaluated the effect of long-range hydrodynamics in dense suspensions. To this end, we have compared full Stokes simulations with widely used molecular dynamics simulations. Our first results on frictionless particles show that there is a slight difference on viscosity although it still diverges similarly (same $\phi^* \approx 0.64$ and similar critical exponent) whether long-range interactions are accounted or not. Frictional simulations are on the way to confirm this behavior.

Wednesday 10:40 Grand Ball

Non-linear viscoelastic behaviour of a suspension of magnetized solid particles under large amplitude oscillatory shear test: A direct numerical simulation

Mohammad R. Hashemi¹, Mehrdad T. Manzari², and Rouhollah Fatehi³

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Magnetorheological fluids are made by suspending micron-sized magnetizable solid particles in a non-magnetic liquid. Upon the application of an external magnetic field, particles are arranged in chain-like clusters which can greatly resist flow. Depending on the intensity of the magnetic field, size, and concentration of the magnetic particles, these chains can span the whole width of the test domain; so that, a solid-like viscoelastic behaviour is observed. By imposing a rather large shear strain, magnetic chains break most probably from their tips, and ultimately a fluid-like behaviour is observed. At this point, magnetic clusters are majorly non-gap-spanning.

In this work, a magnetorheological fluid formed by a series of single-width para-magnetic chains suspended in a Newtonian fluid is studied. The system is confined in a (periodic) channel and its effective stress response is investigated under an oscillatory shear test. Due to limitations of the conventional particle-level simulations, here, a direct numerical simulation approach is employed. It is revealed that the system behaves as a viscoelastic fluid whose moduli depend on the frequency; the storage modulus is an increasing function of frequency while dynamic viscosity is decreasing. Under the large amplitude oscillatory shear test, both the intra-cycle and the global nonlinear behaviour of the system are investigated. It was observed that the system exhibits strain-softening while the trend of the dynamic viscosity alters with the external magnetic field.

Wednesday 11:00 Grand Ball

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Modeling rod suspensions in non-Newtonian fluids by using the slender body theory

Julien Férec¹, Erwan Bertevas², Boo Cheong Khoo², <u>Gilles Ausias¹</u>, and Nhan Phan-Thien² ¹Institut de Recherche Dupuy de Lôme, FRE CNRS 3744, Université de Bretagne-Sud, Lorient 56100, France; ²Department

of Mechanical Engineering, National University of Singapore, Singapore, Singapore

Suspensions of slender particles in liquids are encountered in several natural and engineered products, with particle size ranging from microscopic, down to nanoscopic scale. Such systems represent an important class of non-Newtonian fluids but most of the work found in the literature has focused on the study of rod-filled Newtonian liquids although many unfilled matrices exhibit a non-Newtonian behavior. Hence, the current understanding of the effect of the presence of rods on the composite rheological properties remains incomplete. To tackle this issue, a cell model (or self-consistent scheme) is used to derive constitutive equations for rod suspensions in non-Newtonian viscous matrices such as power-law, Ellis, Carreau and Bingham fluids. It is observed that the shear-thinning character of the matrix influences considerably the rod contribution to the stress tensor, but has no impact on the rod orientation dynamics: the same microstructure evolution as the one encountered in Newtonian fluids is obtained. For a Bingham plastic fluid, the yield stress is found to be proportional to the second-order orientation tensor, which describes the rod orientation state in an efficient and concise way without significant loss of information. As compared to the Newtonian solution based on the Jeffery equation, the orientation time evolution for the particles involves a diffusion term function of the yield stress value of the fluid.

Wednesday 11:20 Grand Ball

Simulations of particle suspensions in shear-thinning and shear-thickening fluids <u>DHIYA ALGHALIBI</u>¹, IMAN LASHGARI², Sarah Hormozi³, and LUCA BRANDT⁴

¹Department of Mechanics, Royal Institute of Technology KTH, Stockholm SE-100 44, Sweden; ²Department of Mechanics, Royal Institute of Technology KTH, Stockholm SE-100 44, Sweden; ³Mechanical Engineering, Ohio University, Athens, OH, United States; ⁴Department of Mechanics, Royal Institute of Technology KTH, Stockholm SE-100 44, Sweden

We study suspensions of non-colloidal spheres in non-Newtonian fluids. Both Carreau and power-low models are employed to describe the rheological behaviour of shear thinning and shear-thickening carrier fluids where the fluid viscosity varies instantaneously with the local flow shear-rate. We use an Immersed Boundary Method to model and evolve the finite-size rigid and neutrally buoyant spherical particles.

The flow is solved in the domain on a fixed Eulerian grid while the presence of each particle is modeled by a set of Lagrangian grid points on its surface. The IBM forcing is calculated on each Lagrangian points to ensure the no-slip and no-penetration boundary conditions. The simulations are performed in a planar Couette configuration where the rheological parameters of the fluid and the particle properties are kept constant while the volume fraction of the solid phase and the bulk shear rate are varied. We aim to test whether the homogenization theory of Chateau [1] for non-Newtonian particle suspensions in the presence of negligible inertia is valid also in our case. Results show that in the lower range of bulk shear rate the behavior of the suspension can be predicted by Carreau models employing a modified shear rate as a function of volume fraction; i.e. the homogenization theory works well. However, at higher shear-rate the effective viscosity of the suspension starts to deviate from the empirical fits due to the inertial shear thickening. Similar behavior is observed for the suspension with power-low fluids in the range of bulk shear-rate investigated. Shear-thinning effects tend to push the particles toward the wall when flow follows the homogenization scaling. Opposite is true for the particle concentration in the inertial shear-thickening regime.

[1] Chateau, X., G. Ovarlez, "Homogenization approach to the behavior of suspensions of noncolloidal particles in yield stress fluids," J. Rheol. 52, 489-506 (2008).

Wednesday 11:40 Grand Ball

SC23

Patterns of neutrally buoyant particles in pressure-driven flow at finite inertia: macroscopic or microscopic origin?

Micheline Abbas¹, Ganesh Subramanian², Olivier Masbernat³, and Eric Climent⁴

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In laminar pressure-driven flow, finite-size neutrally buoyant particles migrate towards the channel walls due to an inertial lift force at sufficiently high channel Reynolds number. Therefore, a moderately concentrated suspension flow, initially homogeneous, becomes stratified into three layers: a central layer of pure fluid in between two suspension layers. Particle-resolved numerical simulations revealed that at long time scale, the stratified suspension is not steady for Re = O(1000). A succession of (streamwise oriented) contra-rotating structures is evidenced, in correlation with the development of concentration waves in the spanwise direction. We are interested in understanding whether the origin of the instability is related to a macroscopic rheology-induced mechanism, or a more microscopic mechanism involving a particle-level lift force. The first scenario is related to second normal stress differences that develop in the suspension layers at finite particle Reynolds number, whereas the particle-free region of the flow is Newtonian. This can lead to differential tension/compression along the base-state vortex lines that are oriented in the spanwise direction, and is responsible for driving an instability. The second scenario is based on a microscopic mechanism involving the action of a shear-induced migration of a single particle. A local deficit in concentration induces a deficit in the local effective viscosity. From momentum conservation arguments based upon suspension effective viscosity fluctuations, the more (resp. less) viscous or concentrated regions have smaller (resp. larger) streamwise velocities when driven by the same pressure drop along the longitudinal direction. In the resulting spanwise varying shear flow (in the flow-vorticity plane), the particles tend to migrate in that plane from the faster flow regions (lower concentration) to the slower ones (higher concentration) due to inertial lift force. This can also lead to the amplification of the perturbation in concentration.

Symposium NF

Non-Newtonian fluid mechanics and fluid instabilities

Organizers: Natalie Germann and Suzanne Fielding

Wednesday 10:00 Amalienborg

NF18

Elastic instabilities in planar extensional flow of viscoelastic fluids in a cross-slot rheometer

Filipe A. Cruz and Manuel A. Alves

Departamento de Engenharia Química, CEFT, Faculdade de Engenharia da Universidade do Porto, Porto 4200-465, Portugal

We perform a computational analysis on the existence and characteristics of elastic instabilities in the flow of FENE-CR fluids in an optimized shape cross-slot extensional rheometer, abbreviated as OSCER device [Haward et al., Phys Rev Lett 109(12):128301, 2012]. Nine fluids with different extensibilities, relaxation times and solvent viscosity ratios are studied, in flows with very low to negligible inertia (Reynolds number below 1 for most of simulations). We identify the following main types of flow instabilities: (1) stationary asymmetries, similar to those observed in the standard, planar cross-slot geometry; (2) time-dependent flow arising from the initial symmetry breaking phenomenon; (3) a second type of time-dependent flow, wherein the flow field is symmetric relative to the outlet axis of the geometry, however the stagnation point oscillates around the central point of the device; (4) a third type of time-dependent flow characterized by a similar oscillation of the stagnation point about a point located some distance downstream of the centre of the OSCER geometry; (5) other instabilities which can be interpreted as a superposition of the above cases. The mechanisms underlying the various instabilities are discussed, as well as the emergence of non-periodic modes of oscillation.

Wednesday 10:20 Amalienborg Vortex formation in a planar elongational flow field: Effect of fluid elasticity

Simon J. Haward¹, Noa Burshtein¹, Konstantinos Zografos², Robert J. Poole², and Amy Q. Shen¹

¹Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan; ²University of Liverpool, Liverpool L69 3GH, United Kingdom

Newtonian flows in the cross-slot geometry undergo a symmetry-breaking bifurcation that results in the formation of a steady spiral vortex structure as the Reynolds number exceeds a modest critical value Re_c [1]. Here we examine how the development of this vortex is influenced by fluid elasticity through the addition of high molecular weight poly(ethylene oxide) (PEO) over a wide range of concentrations 0.0001 < c < 0.1 wt%. The effects of fluid relaxation time ? and viscosity ratio ß are decoupled by using solvents of various viscosity. We perform flow visualization in the cross-slot using fully quantitative micro-particle image velocimetry, from which vorticity fields in the cross-section of the spiral vortex are computed. The vorticity in the centre of the spiral vortex serves as a suitable bifurcation parameter to characterize the growth of the instability with Re. Remarkably, we can observe a significant effect on Re_c (and also upon the vorticity growth for Re > Re_c) at polymer concentrations as low as 0.0001 wt%, i.e. in the concentration regime typically associated with polymer drag reduction [2]. As the polymer concentration is increased, Re_c, and the intensity of the vortex that forms for Re > Re_c, become progressively reduced. At sufficiently high polymer concentrations c > 0.1 wt%, we observe no vortex formation, but we encounter flow asymmetries due to the dominance of elastic effects at high Weissenberg numbers (Wi). Our data can be collapsed to delineate a stability boundary in dimensionless Wi-Re-β parameter space. Our results are qualitatively supported by numerical simulations and constitute new data on stability of low to moderate elasticity fluids in elongational flow fields. Our experimental configuration allows direct and prolonged examination of a single steady vortex, providing new insight into the effects of drag-reducing concentrations of polymer on vortex formation and dynamics.

[1] SJ Haward et al, Phys Rev E 93: 031101 (2016) [2] PS Virk & H Baher, Chem Eng Sci 25: 1183 (1970)

Wednesday 10:40 Amalienborg

Relaxing in a millisecond: scaling of weakly viscoelastic jet thinning

Susanna Formenti¹, Wouter Mathues², Bavand Keshavarz³, Gareth H. McKinley³, and Christian Clasen² ¹Dipartimento CMIC 'Giulio Natta', Politecnico di Milano, Milano, Italy; ²Department of Chemical Engineering, KU Leuven, Leuven, Belgium; ³Department of Mechanical Engineering, Massachussetts Institute of Technology, Cambridge, MA, United States

Weakly viscoelastic fluids are employed in many applications that involve free surface flows, ranging from inkjet printing to fertilizers spraying. Understanding the jet breakup dynamics and the extensional properties of the solutions plays an essential role in determining successful processing conditions. The recently proposed Rayleigh Ohnesorge Jet Elongational Rheometry (ROJER) is suitable to probe the extensional response of such weakly elastic fluids of low viscosity, which are difficult to probe with other techniques like the commonly used Capillary Break-up Extensional Rheometry (CaBER). In CaBER experiments, it has been theoretically predicted and experimentally verified that the filament radius R decreases exponentially with time ($R \propto \exp(-t/3\lambda)$) when the elastic stresses in the filament are sufficiently high to balance the surface tension, enabling the determination of the extensional relaxation time λ . However, in this paper we demonstrate that, while the CaBER experiments exhibit a characteristic time scale of 3λ (which has been utilized so far also for the evaluation of ROJER experiments), a different scaling seems to hold for jetting experiments in ROJER-type setups, independently of experimental and geometrical parameters.

In this paper, we want to give an explanation for this apparent discrepancy, exploiting a novel jetting setup combined with high resolution high-speed imaging. The study of the filament breaking dynamics of model dilute weakly elastic polymer solutions, comparing both jetting and static capillary breakup, as well as theoretical considerations of the correct force balance governing the thinning dynamics, lead to a better understanding of the correct scaling laws and on how to correctly determine millisecond extensional relaxation times.

Wednesday 11:00 Amalienborg

Inviscid-elastic filaments of dilute polymer solutions - an analytical solution for breakup time predictions

<u>Christian Clasen</u>¹, Taisir Shahid¹, Wouter Mathues¹, and Evelyne Van Ruymbeke²

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The applicability of dilute polymer solutions in free surface flow processes that involve a strong extensional component depends to a large extend on the longevity of the filament that forms after the development of a Rayleigh instability on an initial liquid bridge and that connects two consecutively forming droplets. Based on the analysis of V. Entov and J. Hinch [1], the stability and thinning dynamics of this liquid bridge has been described theoretically in great detail, and the predicted dynamics have been confirmed experimentally in several publications. In particular, a recent publication by C. Wagner et al. [2] describes an analytical solution for this elastocapillary (EC) balance regime, that allows a quantitative description of the breakup time for a known relaxation time and finite extensibility of the polymer in solutions, once the onset point of this EC regime I known. However, their analysis for the description of this onset point was based on the assumption of a viscid fluid. Since many dilute polymer in practical applications involve solvents that behave inviscid during filament thinning, we present in this paper an analytical solution for the evolution of the polymer stretch in an inviscid solvent, based on the FENE-P model, that allows us to quantitatively predict the breakup time of inviscid-elastic filaments. In particular, we are presenting for the first time a realistic solution for the polymer stretch evolution in the initial, inertia dominated thinning regime. Predictions of this model are compared to experimental results for a number of model polymer solutions that span the relevant range of intrinsic Deborah and Elastocapillary numbers for actual applications.

[1] V.M. Entov, E.J. Hinch, JNNFM 72 (1997), 31-53. [2] C. Wagner, L. Bourouiba, G.H. McKinley, JNNFM 218 (2015), 53-61.

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Wednesday 11:20 Amalienborg

Capillary Break-up of Liquid-Liquid interfaces: (map of misery)²

<u>Karel Verbeke</u>¹, Susanna Formenti², Francesco Briatico Vangosa², Naveen K. Reddy³, and Christian Clasen¹ ¹Chemical Engineering Department, KU Leuven, Leuven, Belgium; ²Dipartimento CMIC 'Giulio Natta', Politecnico di Milano, Milano, Italy; ³Research Group Packaging Technology Center, Hasselt University, Diepenbeek, Belgium

Studies of capillary breakup phenomena of liquid filaments are classically related to liquid-air interfaces; however, there is a variety of applications where liquid-liquid interfaces are involved. The presence of a surrounding medium of different viscosity and different interfacial tension significantly changes the dynamics, so that the classical descriptions need to be reconsidered. Pioneering studies on this topic focused usually on the thinning and breakup behaviour near pinch-off in dripping experiments, exploiting a large range of viscosity ratios. For this, different similarity solutions were proposed to describe the universal pinch-off for well-defined regimes of the Navier-Stokes equations.

The aim of the current work is to explore the thinning behaviour away from the proposed self-similar final stage of pinch-off for a wide range of inner and outer fluids, combining inertia controlled, viscous and intermediate fluids. To this end, capillary thinning of filaments with liquid-liquid interfaces is investigated, using a modified version of a capillary breakup setup. This novel liquid-in-liquid technique allows to accurately control the instability induced in the filament and to vary the step-stretch profile. A high-resolution optical setup enables to get information about the complete shape of the interface throughout the capillary breakup process.

Results will be presented, focussing on the whole parameter range of inner and outer fluid types, to demonstrate transitions from viscosity controlled to the self-similar thinning for a viscous inner fluid and an inertia-viscous outer fluid. Secondly, we show that the capillary thinning of inviscid fluids can be investigated in higher detail, thanks to the slowed-down dynamics arising from the lower interfacial tension. The proposed framework will pave the way towards studies of active interfaces, stress and deformation rates determination using techniques like particle tracking, X-ray scattering and birefringence in capillary breakup experiments.

Wednesday 11:40 Amalienborg NF23 **Turbulent drag reduction of a flexible polymer in parallel shear flows: correlating CaBER measurements and pressure drop**

Bayode Owolabi, David J. Dennis, and Robert J. Poole

University of Liverpool, Liverpool, United Kingdom

It is well known that high molecular-weight flexible polymers possess excellent drag-reduction (DR) capabilities in turbulent flow when added to a liquid even at minute concentrations. This phenomenon has prompted a large number of studies, yet it has never been possible to relate the degree of DR to a measurable fluid property. A good understanding of their extensional rheological properties is believed to be crucial to obtaining a better insight into their DR mechanism. Until fairly recently, with the introduction of the Capillary Break-up Extensional Rheometer (CaBER), these properties have been elusive to experimentalists (due to the dilute nature of the polymer solutions) [1-2]. Mechanical degradation of polymer molecules is also a major issue [3], giving rise to poor repeatability and large uncertainties in experimental data. In this study, we investigate the relationship between DR and fluid elasticity in channels of circular, square and rectangular cross sections using two grades of polyacrylamide (PAA) solutions having different molecular weights, with concentrations ranging from 150 to 350 ppm. The PAAs were subjected to various levels of degradation by recirculating through the experimental rigs and their relaxation times (?) were determined at different pumping times using CaBER. A plot of %DR against Weissenberg number (Wi=?, γ ; where γ is the average shear rate at the wall) was found to approximately collapse the data, with the onset of DR occurring at Wi 0.5 and the maximum DR asymptote (beyond which %DR is independent of Wi) obtained for Wi ?5. Hence, for the first time, we can make quantitative predictions of DR from the knowledge of a single measurable material property of a polymer solution, independent of other experimental variables, at least for this flexible linear polymer.

Refs.

[2] A. Zell et al JNNFM. 165, 1265-1274 (2010)

[3] J.M.J Den Toonder et al, Appl. Sci. Res., 55:63-82 (1995)

Symposium SM

Polymer solutions and melts

Organizers: Giovanni Ianniruberto and Qian Huang

Wednesday 10:00 Christiansborg **Rheology modification with ring polymers** <u>Dimitris Vlassopoulos</u>

Materials science and technology- University of Crete, Foundation for research and technology-Crete, Heraklion, Greece

Unconcatenated ring polymers with molar mass well above the entanglement threshold, purified via fractionation at the critical condition, relax stress via power-law, sharply departing from their linear counterparts. Concomitantly, their nonlinear shear rheology is also very different from that of unlinked chains and behave akin to FENE Rouse chains and exhibit much small deformation at steady state. Here we focus on blends of rings and linear polymers and show that they exhibit intriguing features in different regimes: The addition of minute amounts of linear chains drastically affects ring dynamics because of the ability of unlinked linear chains to thread rings. This also explain

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^[1] D.F. James, J. Cent. South Univ. Technol. 14 (2007)

the extreme sensitivity of rings to purity issues. In the other end of the spectrum, adding small amounts of rings to linear polymers of different molecular weights greatly influences their linear and nonlinear rheology. The blend viscosity exceeds that of the slower component (linear) in this non-interacting mixture. Its dependence on composition and molecular weight ratio are critically examined, whereas the role of molecular architecture is also addressed. Consequently, the lack of free ends can serve as a powerful means for molecular manipulation of polymer rheology. This presentation reflects collaborative efforts with S. Costanzo, Z-C. Yan, R. Pasquino, M. Kaliva, S. Kamble, Y. Jeong, P. Lutz, J. Allgaier, T. Chang, D. Talikis, V. Mavrantzas and M. Rubinstein.

Wednesday 10:40 Christiansborg

Terminal relaxation behavior of high molecular weight ring polystyrenes

<u>Yuya Doi</u>¹, Atsushi Matsumoto², Tadashi Inoue², Takuro Iwamoto³, Atsushi Takano³, Yushu Matsushita³, Yoshiaki Takahashi⁴, and Hiroshi Watanabe¹

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To elucidate the cause of slow viscoelastic terminal relaxation of high-M ring polymers, rheo-optical and dynamic viscoelastic behavior of high-M ring polystyrene (PS) samples (R-240, M = 244 kg/mol, M/Me ? 14) with different purities was examined. From rheo-optical measurements, R-240 satisfied the stress-optical rule (SOR) in the terminal region and its stress-optical coefficient was indistinguishable from that for of linear PS. This fact suggests that the stress of R-240 chains reflects their orientational anisotropy, as is the case for linear chains. From dynamic viscoelastic measurements of four R-240 samples with different purities, dynamic moduli of R-240 without including any linear contaminations were estimated. The moduli of supposedly pure R-240 were found to exhibit more rapid exponential decay and much broader terminal relaxation mode distribution compared with the models based on the lattice-animal (LA) conformation. The former fact suggests that essentially the models based on the LA conformation are not applicable for actual high-M ring chains. The latter fact suggests that some intermolecular interactions such as ring-ring threading occur for actual high-M ring chains.

Wednesday 11:00 Christiansborg Viscoelastic Relaxation of Mono-functionally End-Associating Rouse Chains: Experimental Test

Hiroshi Watanabe and Yumi Matsumiya

Institute for Chemical Research, Kyoto University, Uji, Kyoto 611-0011, Japan

Viscoelastic test was made for end-calboxylated polyisoprene (PI-COOH) of the molecular weight M = 30.5k that underwent the interchain association and dissociation through hydrogen bonding of the COOH groups at the chain end. As a reference, the test was made also for neat PI unimer (with no COOH group at the chain end) and for PI2 dimer (with M = 61.0k), the latter being synthesized through endcoupling of PI anions (precursor of the PI-COOH sample). The PI-COOH, neat unimer, and dimer samples were diluted in oligomeric butadiene (oB) to a concentration of 10 wt%. The neat unimer and dimer exhibited non-entangled Rouse behavior at this concentration, as expected from their molecular weights. At low temperatures ($T = 0^{\circ}C$) the PI-COOH sample relaxed slower than the reference unimer but faster than the dimer, whereas the relaxation of PI-COOH approached that of the unimer with increasing $T > 0^{\circ}C$, and this change of the relaxation time of PI-COOH was associated with changes in the frequency dependence of the dynamic modulus. This behavior of PI-COOH was well described by a recently proposed theory considering motional coupling between the end-associating unimer and its dimer at chemical equilibrium. On the basis of this result, an effect of the polymeric character of PI-COOH chain on the viscoelastically detected association/dissociation of the hydrogen bonding of the COOH groups was discussed.

Wednesday 11:20 Christiansborg

Morphological Evolution and Dynamic Change of Ionomer/Plasticizer Mixtures during a Transition from Ionomer to Polyelectrolyte

Quan Chen¹, Zhijie Zhang¹, and Ralph H. Colby²

¹State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Changchun, Jilin 130022, China; ²Department of Materials Science and Engineering, State College, PA, United States

For ionomers, unfavorable interaction between highly polar ion pairs and the low polarity polymer medium leads to ion aggregation. In contrast, for polyelectrolytes, the counterions prefer solvation in the polar medium to leave the chain charged and accordingly stretched due to the charge repulsion. In this study, morphological evolution and dynamic change of mixtures of two ionomers with high dielectric constant low volatility plasticizers were examined. The ionomer chains having bulky side chains are not entangled. Upon increasing the plasticizer content, the terminal relaxation is significantly accelerated due to two effects: (1) a plasticizing effect lowering the Tg and (2) a higher dielectric constant that softens the ionic interactions, leading to ionic dissociation into isolated pairs. A model incorporating these two mechanisms predicts quantitatively the accelerated dynamics as ionomers transition to polyelectrolytes on dilution.

Wednesday 11:40 Christiansborg

Following Phase Transitions with Rheometry and Simultaneous Raman-Spectroscopy Jan P. Plog

Material Characterization, Thermo Fisher Scientific, Karlsruhe, Germany

The use of a coupled rheometer and Raman spectrometer for obtaining comprehensive insight into a materials behavior is presented.

Rheology is the analytical method of choice to correlate the absolute flow and deformation characteristics of a given material with its behavior towards a certain processing or application step. However, Rheology as an integral method only yields answers on the bulk of the investigated sample. It does not give any insights into what is actually happening on the molecular level when rheological changes are observed.

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Raman spectroscopy has shown its ability as a powerful, effective and non-invasive method for chemical analysis. Coupling a rheometer with a Raman spectrometer provides direct information about the molecular reaction kinetics and the mechanical properties. This is extremely useful for studying phase transition behavior like i.e. the crystallization behavior of polymer melts during processing. It can also provide insight for in-situ characterization and monitoring which can be challenging when working with on-line techniques as only relative flow fields are characterized.

Finally, the coupling gives the researcher the advantage of maximizing and synchronizing the information gathered from a single measurement as well as enabling transient information on their materials during fast processing conditions.

In this contribution we present results obtained with the new combination of a Thermo Scientific HAAKE MARS rheometer with a Thermo Scientific Raman spectrometer. Details of this unique set-up as well as selected results will be presented.

Symposium FB

Food and biorheology

Organizers: Henrik Kragh and Ulf Andersen

Wednesday 10:00 Fredensborg

Rheology of co-amorphous drug-drug melts with and without polymeric additives

Lærke Ø. Arnfast, Johanna Aho, and Jukka Rantanen

Department of Pharmacy, University of Copenhagen, Copenhagen, Denmark

Excipient selection for melt-based pharmaceutical products needs to consider not only processability and product performance but also limitations in terms of acceptable product size. The aim of this study was to study the effect of polymer type, grade and concentration on rheological properties of highly concentrated molten drug-drug mixtures. Physical mixtures of indomethacin and cimetidine (IND-CIM, 1:1 molar ratio) and indomethacin and naproxen (IND-NAP, 1:1 molar ratio) were used as model drug-drug systems. Polyethylene oxide (PEO, Mv 100.000, 300.000 and 1.000.000) and polyvinylpyrrolidone (PVP, Kollidon 12 and 17) were used as polymeric additives. Physical mixtures with polymer contents of 0-20 w/w% were analysed in small amplitude oscillatory shear. Melts of IND-CIM at 120 °C display a highly viscous response increasing in viscous dominance with increasing frequency (tan(d) > 10 at 10 rad/s). Addition of 5% PEO 100.000 decreases the viscosity, tan(d), and its frequency dependence (tan(d) ~ 3.5 at 10 rad/s). Addition of PEO of 300.000 and 1.000.000 Mv results in similar effects with an increasingly higher viscosity and lower tan(d), the higher the MV of the polymer. Addition of 5% PVP to IND-CIM increases the viscosity slightly but does not change the effect of frequency on the response of the sample. Again higher molecular weight of the polymer increases the viscosity and lowers the tan(d) of the melt (tan(d) = 8-9 at 10 rad/s). Melts of NAP-IND were too low viscous for a rigorous analysis with the used setup (25 mm plate-plate), however addition of 10% PEO of Mv 1.000.000 enabled testing at 140 °C. Increasing the concentration of this polymer within the investigated range in the IND-NAP system seems to increase the viscosity in a linear fashion. The rheological properties of the studied model systems could be altered significantly with low amounts of polymer, which suggests that also high-dose and/or combinational drug products can be manufactured with melt-based processes at an acceptable unit size.

Wednesday 10:20 Fredensborg

Mucoadhesion using small deformation rheology revisited

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Until now, mucoadhesion of drug delivery systems (DDS) and single excipients components hereof have been evaluated by measuring the change in apparent viscosity upon mixing a mucin suspension with the relevant test sample, compared to a mucin reference sample [1-3]. However, by development of a biocompatible mucus we have shown that it is not only the mucin strains that are important for interactions with DDS, but also that the steric matrix of the mucus itself is crucial [4]. Thus, we hypothesize, that applying biocompatible mucus matrices instead of mucin suspensions for assessment of mucoadhesion will increase the in vivo relevance of the experiment. After mixing biocompatible mucus, porcine intestinal mucus and mucus components, respectively, with commonly used DDS components e.g. chitosan, sucrose acetate isobutyrate, hyaluronic acid, alginate and polyvinyl pyrrolidone, a steady state flow step was performed (ARES-G2 rheometer with a peltier plate and 20mm cone, TA Instruments, New Castle, DE) [4]. Mucoadhesion was defined as an increase in the viscosity eg. ?a>0. As previously described [2,3], ?a is calculated by: ?a=?t-?m-?p where ?t is the total viscosity of the system, ?m the viscosity of mucus sample and ?p the viscosity of the test sample. The data showed a significant increase in ?a when assessing mucoadhesion using biocompatible mucus compared to a mucin suspension. Thus, the mucoadhesive properties of the components tested can be more clearly distinguished from each other hence a more detailed characterization conducted. Conclusively, we have confirmed the hypothesis stating that biocompatible mucus serves as a better model system as compared to mucin suspension, when evaluation mucoadhesion using small deformation rheology. Moreover, we have shown a more reproducible assessment of mucoadhesion when using biocompatible mucus compared to mucin suspension.

[1]doi:10.1111/j.2042-7158.1996.tb00736.x; [2]doi:10.1023/A:1015812615635; [3]doi:10.1016/j.colsurfb.2011.12.020; [4]doi:10.1016/j.ejpb.2015.01.014.

FB19

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Wednesday 10:40 Fredensborg Rheology of living bioinks used in 3D printing

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Despite recent advances in 3D printing of cell-loaded scaffolds for biomedical applications, specific cell localization into complex 3D geometries without a loss of printing accuracy remains a major challenge. Here we report on a 3D printing platform that, besides freeform shaping, enables the digital fabrication of cell-laden hydrogels with full control over the spatial distribution and concentration of cells in complex 3D architectures.

For 3D printing we use a recently developed multimaterial direct ink writing technique(1) which allows us to incorporate various types of cells in biocompatible hydrogel inks within the same 3D printed material. To obtain accurate 3D printed structures, we determine the ideal rheological properties prior, during and after printing, demonstrating the effect of the printing steps on the bioink. In a pre-characterization step, we study the viscosity and viscoelastic properties of our bioinks, revealing shear thinning that is ideal for extrusion based printing, and viscoelasticity for structure retention in 3D printing. With alternating shear rate and oscillation cycles, we mimic the printing process and determine the bioink viscous and elastic recovery after deposition on the substrate. With this approach we are able to obtain a hydrogel which supports cell growth while still maintaining a high shape fidelity in 3D printing.

As a proof of concept, highlighting the importance of rheology in 3D printing, we demonstrate that cell proliferation is a function of viscosity and oxygen availability. By fine-tuning the single ink components, we adjust the viscosity to match the growth profile of our cells. With this versatile printing platform we envision the use of additive manufacturing materials combined together with cells to be used for new and biomedical applications.

(1) Kokkinis, D., Schaffner, M. & Studart, A. R. Multimaterial magnetically assisted 3D printing of composite materials. Nat Commun 6, (2015).

Wednesday 11:00 Fredensborg

Predicting Structure, Diffusion and Viscosity in Therapeutic Antibody Solutions

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Therapeutic antibodies represent the fastest growing segment of the biopharmaceutical industry. Their application to treatment of cancers and autoimmune diseases is prolific. The engineering of antibodies, processes for their production, and mechanisms for administration is of intense scientific interest. Because of their sequence specific, heterogeneous charge distribution, antibodies can interact strongly, which has a significant impact on solution rheology. The viscosity of antibody solutions is a key parameter and constraint on processes such as ultrafiltration and administration routes such as subcutaneous or intravitreal injection. No methods exist currently to predict the rheology and dynamics of concentrated antibody solutions. I will present the results of a study of two antibodies via coarse-grained simulations. The simulations incorporate hydrodynamic interactions between the suspended proteins as well as appropriate colloidal interactions among the coarse-grained domains. The simulations reproduce the static structure factor of each antibody measured via neutron scattering, and different estimates of the intermolecular friction are used bound the short-time self-diffusivity measured via neutron spin echo. The shear stress autocorrelation function and the zero shear viscosity are computed. Good agreement is found with the measured viscosity of one of the antibodies. However, the simulations significantly underestimate the viscosity of the other antibody. This too can be attributed to uncertainty in the intermolecular friction and suggests potential avenues for future investigation.

Wednesday 11:20 Fredensborg

A new look at blood shear-thinning

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Blood viscosity decreases with shear stress, a property essential for an efficient perfusion of the vascular tree by the heart. This shearthinning property is intimately related to the dynamics and mutual interactions of its major constituents, the red blood cells (RBCs). At shear stresses relevant for the microcirculation, shear-thinning has been interpreted in the framework of emulsion rheology. In this picture, RBCs should align and elongate in the flow direction while their membrane would circulate similarly to a tank tread, reducing flow-line disturbances. However, tank-treading has only been observed when RBCs are dispersed in media with a viscosity much greater than the one of the suspending plasma. Due to the lack of knowledge about RBC behavior under physiological conditions, the link between cellularscale dynamics and shear-thinning remains unsettled. Using both experiments and simulations, we show that blood shear-thinning is the result of a rich dynamic behavior of RBCs convoluted with a large distribution of shapes for any given flow condition. For increasing shear stresses, RBCs successively tumble, roll, deform into rolling stomatocytes and finally adopt highly deformed and polylobed shapes without clear tank-treading of their membrane. The lack of membrane fluidity is the key feature which controls morphological transitions and therefore global rheological behavior.

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Wednesday 11:40 Fredensborg

Thixotropy of blood as a measure of red blood cell aggregation

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Blood composes cells-which have different size, shape, and functionality-that are embedded into a colloidal solution-the blood plasma. Blood responds to external strain on a species-specific basis. Forces between red blood cells (RBCs) and between RBCs and surrounding plasma molecules are low, but can be quantified by small amplitude oscillation (yield stress: 5-15 mPa at 1.5 s-1). However, if RBC aggregability is low (domestic ruminants and many rodents) G'-values cannot be detected at physiological hematocrit (HCT). The suspension needs an increment of RBCs to gain elastic behaviour. At high RBC aggregation (in healthy horses due to increased RBC aggregability, or during inflammatory disease in man) G'-values can be measured at low HCT, but thixotropy of blood is pronounced. This can perturb the homogenous flow needed for correct readings, especially if long time intervals are set. By measuring dynamic shear viscosity of whole blood (WBV) at predefined temperature increments we observed that WBV did not decrease monotonically when temperature was raised. Instead, there was a sudden WBV step at a certain temperature. We hypothesize that a specific superstructure is built passing a temperature cut-off. There was clear relation to RBC aggregation. For instance, in horse blood or in human blood at elevated plasma fibrinogen concentration, this effect was pronounced. In contrast, in sheep or camel blood where RBC aggregability is lacking, there was no such effect. WBV shifted in parallel with the increase and decrease of temperature. However, when the measurements started above the cut-off-temperature (f.i. at physiological body temperature of 37°C) to measure flow curves while the sample was cooled, WBV shifted monotonically with the temperature drop. This indicates that a superstructure is stabilized, once it is formed above the temperature cut-off. The relevance of this finding has to be elucidated, but its clear relation to RBC aggregation makes it useful as a measure for RBC aggregation.

Symposium SG

Solids, glasses, and composites

Organizers: Jeppe C. Dyre and Esmaeil Narimissa

Wednesday 10:00 Kronborg

Photochemical reactivity of PLA at the vicinity of glass transition temperature

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The glass transition temperature (Tg) is one of the most important structural and technical characteristics of polymeric materials which determines their range of applications. Below Tg the material is brittle, whereas above this point it is more flexible like rubber or liquid. Those properties depend on molar mass of the polymer chains, its crystallinity and degree of crosslinking. The correlations of Tg of polymers with their chemical composition, molecular weight, rigidity and symmetry of chains, as well as some other characteristics of macromolecules were frequently and comprehensively presented⁽¹⁾.

A photo-rheology method⁽²⁾ was applied to determine photochemical reactivity of poly(lactic acid) (PLA) close to glass transition region. The differences in the rheological behaviour were measured during in situ UV irradiation in air. At low frequency (1 rad s⁻¹), the highest reactivity was observed at the glass transition temperature (about 57 °C) which corresponds to the data from DSC. Below and above this temperature, the rate of PLA chain scission degradation was lower. Because the range of temperature is relatively low (50-70 °C), thermal decomposition of hydroperoxides doesn't occur, so only effect of UV irradiation can be observed.

Moreover, it was also shown that changing the oscillation frequency led to the maximal rate of the chain scission rate occurring at temperatures slightly higher (shifted due to time-temperature superposition effects).

 J. Bicerano, Prediction of Polymer Properties, third ed., Marcel Dekker, INC., New York, 2002, pp. 157-240.
 Molecular Evolution of Polymers through Photoageing: A New UV in situ Viscoelastic Technique. V. Verney, S. Commereuc, Macromol. Rapid Commun. 2005, 26, 868-873

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Wednesday 10:20 Kronborg

SG18

Rheological and electrical properties of polymer nanocomposites incorporated with surface-modified CNTs Jae Phil Song, Jun Young Kim, and Seong Jae Lee

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Carbon nanotubes (CNTs) are used as conducting nanoscale fillers to enhance the electrical performance of polymer nanocomposites due to their outstanding electrical properties and thermal stability. However, it very difficult to disperse CNTs in a polymer matrix as they have large van der Waals forces tending to bundle together. A lot of attempts such as physical and chemical modifications of CNTs have been made to solve the dispersion-related problems. Chemically modified CNTs show good dispersion but deteriorate the intrinsic properties of CNTs by the breakage of sp2 bonds. Physical modification with low molecular weight surfactant renders good dispersion but shows

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adverse effect on mechanical properties of nanocomposites. In this study, polystyrene (PS)/surface-modified CNT nanocomposites were prepared by latex technology, and then rheological and electrical properties of the nanocomposites were investigated to compare the effect of surface modification. Polydopamine coated CNTs (PDA-CNTs), poly(3,4-ethylenedioxythiophene):poly(4-styrenesulfonate) coated CNTs (PEDOT:PSS-CNTs), and sodium dodecyl sulfate stabilized CNTs (SDS-CNTs) were used as nanoscale fillers. PDA-CNTs were prepared by spontaneous oxidative polymerization under tris-HCl buffer solution, and PEDOT:PSS-CNTs were prepared by p-p stacking interaction between PEDOT:PSS and CNT. Good dispersions of surface-modified CNTs in aqueous PS latex system were achieved, and consequently rheological properties of all the nanocomposites were substantially increased with small addition of the CNTs, which indicated the formation of physical networks. Highly enhanced electrical properties were also obtained with the electrical percolation threshold of less than 1 wt%. PS/PEDOT:PSS nanocomposites showed higher conductivity than PS/PDA counterparts due to the good electrical properties of PEDOT:PSS.

Wednesday 10:40 Kronborg

SG19

Micromechanics of spongy-particle systems: Approach towards equilibrium Monica E. A. Zakhari, Patrick Anderson, and Markus Hütter

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Open-porous deformable particles, often envisaged as sponges, are ubiquitous in biological and industrial systems (e.g. casein micelles in dairy products and microgels in cosmetics). The material of the supporting network gives rise to elastic behavior of the particles, while the viscous permeating solvent gives rise to their rate-dependent behavior. Modeling the rate-dependent behavior of such particles requires taking into account the structure of the particle, i.e. its permeability. Using the general equation for the nonequilibrium reversible-irreversible coupling (GENERIC)¹, a concurrent two-scale model has been developed which accounts for the particle rate-dependence by treating the particle-size as a separate degree of freedom². This work applies this model to spongy-particle suspensions with the aim of studying the effect of particle permeability on the overall mechanical behavior. Based on the theory of poroelasticity, we show how the particle-size relaxation is related to the particle permeability. With increasing packing fraction, the mobility of these particles in suspension is drastically decreased, and they undergo a transition to an ordered state at timescales significantly larger than the Brownian timescale, irrespective of the permeability. We find that the transition time depends significantly on the sample history, while the final energy state and stress do not. At times larger than the transition time, we characterize the structure and dynamics of dense suspensions of spongy particles as a function of particle permeability. We show that size-dynamics is important at packing fractions above 80%, and that it accelerates the crystallization process.

This research forms part of the research programme of the Dutch Polymer Institute (DPI), project #738.

¹ Öttinger, H. C., 2005. Beyond Equilibrium Thermodynamics, Wiley Interscience.

² Hütter, M., Faber, T. J., Wyss, H. M., 2012. Faraday Discuss., 158, 407-424.

Wednesday 11:00 Kronborg

Effect of temperature and flyash replacement on rheological behaviour of cement paste during early hydration

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The recent revolution in the concrete industry with the implementation of 3D-printing technique requires an in depth understanding of physicochemical phenomena that take place on micro-structure levels and subsequent rheological behavior during cement hydration. The effects of fly ash and hydration temperatures on the rheokinetics of cement paste were investigated. Two different cements of the same type CEM I 52.5 N and one type of fly ash supplied by a local company were used in this research. Different mixes were considered by partially replacing the cement with fly ash at a rate of 10%. The cement hydration kinetics was characterised by measuring the evolution of the elastic modulus under small amplitude oscillatory shear. The rigidification time and the hydration rate constant of the cement paste were deduced directly from the experimental data. The strength rate of the cement microstructure was estimated by taking into consideration the corresponding retardation and rigidification times. It was found that the formation and the development of the internal microstructure depend strongly on both the hydration temperature and fly ash concentrations. The regidification times of the internal network are related to the hydration rate constant and are both affected by the amount of cement replaced and the curing temperature. The strength rates of the microstructure are not affected at low fly ash replacement (10%-30%). These rheokinetics performances are very specific for each cement used, possibly due to their physical and chemical characteristics.

Wednesday 11:20 Kronborg

SG21

SG20

Is shear-thickening behavior ensuring always the maximum performance in reinforced CorkSTFµfluidic composites?

Francisco J. Galindo-Rosales

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In the last years we all witnessed how shear-thickening behavior was massively used for developing passive composites with improved protective performance under different impact conditions[1]. One example of these composites are the *CorkSTFµfluidic* composites[2], which consist of a sandwich of micro-agglomerated cork laminas, having embedded a microfluidic pattern filled with a shear-thickening

fluid. The fact of using microfluidic channels allows an enhanced shear-thickening behaviour due to its confinement inside the microfluidic channel [3] and the possibility of optimizing numerically design the pattern [4] in order to maximize the damping of the composite.

In this study it is wondered if one really need always to use a shear-thickening fluid in order to ensure the maximum protection of a reinforced composite. Thus, two set of $CorkSTF\mu$ fluidic composites were designed, both consisting of 16 different configurations of parallel straight microchannels, but one filled with a shear thickening fluid and another one filled with a shear thinning fluid. Low velocity impact tests were performed and the results surprisingly showed that in most of the microfluidic pattern configurations, the maximum of the pick force was smaller for the shear thinning fluid than for the shear thickening fluid. These results allowed to infer that using a shear thickening fluid in a reinforced composite when protecting against impacts does not always lead to the best solution. The choose of the right complex fluid must be done wisely taking into account the configuration of the microfluidic pattern.

[1] F.J. Galindo-Rosales. Appl. Sci., 6, 206 (2016).

[2] F.J. Galindo-Rosales et al. Mat. & Des., 82 (5) 326-334.

[3] E. Brown and H.M. Jaeger. Rep. Prog. Phys. 77 (2014) 046602.

[4] F.J. Galindo-Rosales et al. RSC Adv., 4 (2014) 7799-7804.

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Wednesday 11:40 Kronborg

SG22

Rheology as a fast tool to quantify the cross-link density in polyethylenes cross-linked using different crosslinking technologies

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Cross-linking of polyethylene is a way to improve the polymer's properties with respect to e.g. creep resistance or higher continuous operating temperatures. Therefore, cross-linked polyethylene (PE-X) is of interest in a number of industries like cable&wire or pipe. Consequently, the degree of crosslinking is one of the key parameters which has to be documented in quality control. Today, it is determined as gel content by solvent extraction according to DIN EN ISO 10147. This procedure is no longer state of the art as it is time consuming and uses hazardous chemicals. As cross-linked PE behaves as a rubber above the melting temperature scaling laws for rubber can be used. Therefore, G' of an elastomer at absolute temperature T scales linearly with the cross-link density nv (see e.g. [1]) A first attempt to use this correlation for PE-X materials was published by Burhin et al. [2]. Details on the experimental protocol and the factors influencing the results are published elsewhere [3]. The frequency dependence of the storage modulus G' for various cross-link densities for the three crosslinking technologies used in industry resulting in either PE-Xa (peroxide based), PE-Xb (silanol based), or PE-Xc (gamma irradiated) is reported. The moduli increase with increasing frequency as a power-law in all cases. Furthermore, they increase with increasing degree of cross-linking as expected and increase linearly with absolute temperature. A non-linear scaling law (polynomial of degree 2) between the gel content via solvent extraction and the rheological data was established successfully irrespective of the cross-linking technologies. However, it is shown that different scaling parameters have to be applied for the individual cross-linking procedures. Comparing the time necessary to determine the crosslink density the rheological methods yields results within 5 min while the solvent extraction takes 12 hours.

Symposium MN

Micro and nanorheology, microfluidics

Organizers: Eric M. Furst and Anke Lindner

Wednesday 10:00 Schackenborg

MN1

Flow disturbance by an asymmetric particle in a quasi-2D microfluidic channel – simulation and experiments

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Microparticles flowing in confined microfluidic channels are commonly encountered in a wide range of applications - from cell sorting to advanced materials synthesis. These applications have created a demand for techniques to control the motion of flowing microparticles. Tuning the particle dynamics requires in-depth understanding of the hydrodynamic interactions between the particles and the surrounding boundaries. These interactions arise due to a disturbance of the flow field of the carrier fluid, caused by the suspended particles. A theoretical framework has been developed recently to model this phenomenon in microfluidic channels [1][2]. In the current work, we investigate the nature of the flow disturbance field via both simulations and experiments. Our model particle is a dumbbell which consists of two discs held together by a rigid shaft and is confined between the horizontal walls of a slit-like microchannel. Two thin lubrication layers separate the particle from the walls and give rise to additional drag. Thus the dumbbell lags the mean velocity of the surrounding fluid, which gives rise to the flow disturbance field. Our main goal is to quantitatively determine how system parameters such as the lubrication layer thickness and disk size dictate the magnitude of the flow disturbance field, hence their effect on the dynamics of the dumbbell. To this end, we first simulate the motion of the particle in a microchannel using the Lattice Boltzmann method, a popular coarse-

grained technique for complex fluids, as implemented in ESPResSo [3]. We then compare our simulation results to experiments and draw quantitative conclusions. The insight gained enables future study of the collective dynamics of particle ensembles.

References:

W. E. Uspal & P. S. Doyle, Soft Matter, 10, 5177 (2014)
 W. E. Uspal, H. B. Eral & P. S. Doyle, Nat Comm, 4, 2666 (2013)
 D. Roehma & A. Arnold, Eur. Phys. J. Special Topics, 210, 89 (2012)

Wednesday 10:20 Schackenborg

Particle migration in a pillared microchannel

<u>Rohit V. Maitri</u>¹, Shauvik De¹, Shane Koesen¹, John van der Schaaf¹, Frank Peters¹, Johan T. Padding², and Hans Kuipers¹ ¹Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands; ²TU Delft, Delft, The Netherlands

Controlled particle migration in non-Newtonian fluids is very important in many biological, environmental and industrial applications like hydraulic fracturing. The phenomenon of particle transport in non-Newtonian fluid is generally governed by complex interplay of different effects like shear-thinning or thickening behaviour of fluid, viscoelasticity and secondary flow. The present literature on the particle migration in a channel shows that particles move towards the centreline in highly viscoelastic fluids at very low Reynolds number (negligible inertial effects) and move away from the centreline in Newtonian fluids. However, very little is known about how flow and particle dynamics is affected in a rock fracture network or porous medium. To obtain insights into flow dynamics in such a complex geometries, we use microchannels with the specific arrangement of pillars in order to mimic the hydraulic fracture network and porous media. In this study, we perform experiments on the migration of non-Brownian particles in such pillared microchannel of different porosities with different types of fluids - Newtonian, shear-thinning and viscoelastic. The comparison of the particle behaviour in these fluids reveals the influence of the viscous and elastic forces on particle migration. In this work, standard micro-PIV technique is used to obtain the fluid velocity and PTV is used to track the particle velocities. This work provides fundamental insight on effect of viscoelasticity on particle migration in a model fracture network/porous media.

Wednesday 10:40 Schackenborg

The effect of slip on the dynamics of a spherical particle in viscoelastic Poiseuille flow

Marco Trofa¹, Gaetano D'Avino¹, Martien A. Hulsen², Francesco Greco³, and Pier Luca Maffettone¹

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Cross-streamline particle migration, i.e. the motion of particles transversally to the main flow direction, is a well-known and widely studied phenomenon occurring in flowing suspensions. Furthermore, with the recent development of microfluidic chips, the need of controlling particle trajectories has directed the scientific interest in designing novel devices able to induce the lateral motion. In most of the theoretical and numerical studies on the dynamics of rigid particles, the validity of the no-slip boundary condition at all solid-fluid interfaces is assumed. However, at small scales and with complex fluids, boundary slip, i.e., a discrepancy between the fluid velocity and the velocity of the solid surface immediately in contact with it, may occur. Slip at a solid-fluid interface modifies both the fluid velocity profile and the fluid-particle hydrodynamic interactions, affecting, in turn, the particle migration phenomenon. In this contribution, we address the effect of slip on the dynamics of a spherical particle suspended in an inertialess viscoelastic shear-thinning fluid under Poiseuille flow. The study is performed through 3D direct finite element simulations by employing an Arbitrary Lagrangian-Eulerian method for the particle motion. We found that both wall and particle slip qualitatively change the migration dynamics as compared to the no-slip case. Indeed, for sufficiently high slip coefficients, the tube wall becomes an unstable equilibrium position, and the particle migrates toward the tube axis for any initial position. Thus, boundary slip promotes particle alignment and can be exploited to enhance focusing operations in microfluidics.

Wednesday 11:00 Schackenborg

Partial wetting of 2D topography by a viscoelastic film

Dionisis Pettas, Yannis Dimakopoulos, and John Tsamopoulos

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In coating processes driven either by centripetal acceleration (spin coating) or gravity (Nusselt-type of flow) a resin coats the substrate leaving a thin film on it. In such operations many irregularities may arise that have impact on the film thickness due to the micro-structure of the substrate which may contain slits, sharp steps, trenches, pillars and corrugations, the order of which is a few hundreds of microns. The thickness variations additionally depend on the physical properties of the resin (viscosity, elasticity, surface tension, shear thinning) and the flow parameters. The purpose of this work is to examine this dependence as well as the different wetting states of a slit or a trench between complete coating and non-coating of the trench, the Wenzel and Cassie states, respectively. We consider the viscoelastic film flow along an inclined plane, featuring a slit and we allow for the existence of a second gas-liquid interface connecting the two side-walls of the slit. This inner interface forms two three-phase contact lines and supports a widely varying amount of liquid under different physical and geometrical conditions. The liquid of the film follows the exponential Phan-Thien-Tanner constitutive model. We employ the mixed finite element method combined with an elliptic grid generator to account for the highly deformable liquid domain. We find that the interplay of inertia, viscoelasticity and gravity along with the substrate wettability and orientation with respect to gravity and the width of the slit determine the extent of liquid penetration and free surface deformation. Conditions for multiple steady solutions under the same parameter values, which are connected by turning points, are revealed using pseudo arc-length continuation. Then, a small change in certain parameter values leads to an abrupt change in liquid penetration and deformation amplitude of the outer film surface, through hydrodynamic hysteresis.

MN2

MN4

MN3

Wednesday 11:20 Schackenborg

Flow induced microstructure of non Newtonian emulsions in confined capllary flow

Valentina Preziosi, Giovanna Tomaiuolo, <u>Sergio Caserta</u>, and Stefano Guido

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Despite the extensive literature available on the topic, liquid-liquid mixing is still one of the most difficult and least understood mixing problems, especially when one of the two phases shows a non-Newtonian behavior. Non-Newtonian fluids can have elastic behavior and at the same time exhibit nonlinear viscous effects like shear-thinning of the viscosity, it is particularly difficult to study viscoelastic flows in isolation from other effects. A case of special interest arises when some elasticity is introduced by adding small concentrations of high-molecular weight components to the continuous phase (thus making a so called Boger fluid). Such fluids are particularly important because their viscosity behavior is nearly constant with the shear rate even showing significant elastic stresses, thus making them suitable to enable elastic effects to be probed separately from viscous ones. In this work, we focus on the effect of matrix elasticity of low viscosity oil/water emulsions in a confined flow apparatus. Newtonian and two elastic non-Newtonian fluids (Boger fluids), respectively. A direct comparison of the fluid dynamic behavior of Boger fluids compared to the one of Newtonian fluids, at the same Reynolds number, allowed us to isolate the influence of matrix elasticity on emulsion morphology. In all the experiments, a droplet-free layer can be observed close to the wall, since larger droplets accumulate toward the channel axis, while smaller droplets are marginated in an intermediate region. The droplet-free layer is tunable with fluid elasticity, and it could be exploited as a mechanism to separate the two emulsion phases in a flow device.

Wednesday 11:40 Schackenborg

Dynamics of 2D bubbles in a Hele-Shaw cell

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Droplet-based microfluidics is a growing field often requiring an accurate synchronization for automated systems. The question we address is the prediction of a bubble velocity pushed by a surrounding liquid set at a fixed mean velocity. Our understanding of the dynamics of travelling bubbles or droplets in confined geometries has been steadily refined since the pioneering work of Taylor and Saffman, who derived analytically the velocity of a quasi-2D bubble using depth-averaged Hele-Shaw equations [Q. J. Mech.Appl. Math. 12, 265 (1959)]. All the refined reported models, which take into account the dissipation at the meniscus, are 2D [Cantat.,Phys.Fluids 25,031303 (2013)]. However, predicting accurately bubble velocity calls for a full knowledge of the dissipation mechanisms at play, which requires determining the full 3D profile of a traveling bubble, mostly close to the walls. The experimental set up is a microfluidic system in which bubbles flow in fluorinated oil (FC-40) in a Hele-Shaw geometry in a total wetting case, i.e. there is a lubrication film of fluorinated oil between the bubble and the wall. We reported recently an experimental characterization of the lubrication film thickness with an accuracy of 2 nm using RICM [Huerre et al., Phys. Rev. Lett. 115, 064501 (2015)]. In the present work, the bubble velocity. In the present work, we propose a model that takes into account both the viscous dissipation in the menisci and the 3D topography of the lubrication film. Remarkably, this model allows recovering the experimental bubble velocity without any fitting parameter.

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Annual European Rheology Conference 2017

Wednesday Afternoon

Symposium SC

Suspensions and colloids

Organizers: Norbert Willenbacher and Philippe Coussot

Grand Ball Wednesday 13:00

SC24 Relations between colloidal structures in aqueous suspensions based on silica, starch and PEO-PPO-PEO block copolymer and structures of the corresponding composites

Lars Järnström, Yana Petkova-Olsson, and Henrik Ullsten

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Structures in aqueous suspensions based on dispersed colloidal silica and dissolved starch, glycerol and poloxamer (block copolymer of PEO-PPO-PEO type) were studied by scaling relations of rheological parameters vs. volume fraction of particles (φ). Structures of the corresponding dry composites were studied by means of optical microscopy, scanning electron microscopy and confocal Raman microscopy. The temperature at measurements and drying ranged from 20 to 30°C. Flow curves recorded at steady state above a critical shear rate was used to determine the floc volume ratio C_{fp} given by $C_{fp}=\phi_f\phi$, where ϕ_f is the volume fraction of flocs calculated from slightly modified Krieger-Dougherty equation. At φ <0.16 and 30°C, the floc volume ratio decreased strongly with increasing φ , while the opposite was observed at $\varphi > 0.16$ for all temperatures. Small-amplitude oscillatory shear were used to record storage modulus, G' vs. φ . The results revealed the existence two different regions and a transition between the regions at $\varphi \approx 0.16$. In each of the regions the data points were fitted to a power law equation where the exponent represented the microstructure of the suspension. Low values of the exponent was observed at the highest temperature and φ <0.16. The scaling relations as well as other rheological parameters indicated a transition from a colloidal gel (or a liquid-like state at low temperatures) to a colloidal glass at rather low particle concentrations, which is likely for systems with long-range electrostatic interactions. The observed behaviour was a consequence of the temperature-responsive properties of poloxamers. The structures of the dry composites prepared at different particle concentrations and temperatures were explained in terms of results from the rheological study, which indicates the possibility to use rheology as a tool to predict the structures in the final composites.

Wednesday 13:20 Grand Ball

Rheology of screen-printing pastes and their continuous phase

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Front side metallization of Si solar cells is usually realized using traditional screen-printing. Flow properties of screen-printing pastes have to be carefully adjusted to ensure uninterrupted processing. This is challenging since line patterns <35µm have to be achieved. A high yield stress ensures good shape accuracy. A low viscosity at high shear rates is required for paste flowing through narrow mesh openings. The characterization of different process relevant rheological parameters is essential in order to improve processing and product features. We present experimental protocols allowing for reliable determination of yield stress, viscosity, wall slip velocity, structural recovery, elongation at break and tensile force during filament stretching. Yield stress τ_y can be obtained either using a vane or plate-plate geometry for selected plate roughness. Slip increases linearly with τ for $\tau < \tau_y$. The maximum slip velocity can be quantified by the elastohydrodynamic model of Meeker et al. including pastes yield strain, elastic modulus, solvent viscosity, particle radius and modulus. At $\tau > \tau_{v}$ wall slip is of minor relevance and deformation at the sample rim is uniform. This allows the determination of an apparent viscosity at a narrow shear rate or stress range since sample spill sets in at a critical angular speed. This spill occurs in silver pastes but not in the proper particle free continuous phase and is presumably controlled by the balance of centrifugal force and friction at the wall. Structural recovery experiments combining linear and non-linear oscillation reveal an irreversible structural change depending on the amplitude of shear deformation. Elongation at break and its maximum force are parameters may be related to the screen snap-off during printing. Significant differences among various silver pastes and corresponding continuous phase are observed and rheological parameters discussed above will be correlated with printing results.

Wednesday 13:40 Grand Ball

Elasticity and yielding of calcite paste: scaling laws in a dense colloidal suspension

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Calcite is the most stable polymorph of calcium carbonate (CaCO3) and an extremely widespread mineral. The mechanical properties of calcite and its availability make it one of the most widely used minerals as a construction material, abrasive, agricultural soil treatment, and

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more. We address here the mechanical characterization of calcite paste as a model system to investigate the relation between surface interactions and macroscopic behavior of colloidal suspensions, the ultimate goal being to achieve a control of the elastic and flow properties of calcite. Rheological measurements have been performed on calcite suspensions for a wide range of particle concentrations. The calcite paste exhibits a typical colloidal gel behavior, with a solid-like regime (characterized by a linear elastic domain) and a clear yield strain above which it enters a liquid-like regime. The yield strain shows a minimum when increasing the solid concentration, together with a change of the power law increase of the storage modulus. The calcite behavior validates, for the first time without external forcing, the classical fractal elasticity model for colloidal suspensions of Shih et al. [Shih et al., Phys.Rev. A, 1990, 42, 4772].

Wednesday 14:00 Grand Ball

Tunable discontinuous shear thickening in a magnetorheological suspension

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Very concentrated suspensions of carbonyl iron particles in water can be obtained thanks to the use of superplasticizer molecules used in cement industry. At volume fraction around 60% these suspensions show a discontinuous shear thickening (DST) behavior which is quite similar to the one observed on aqueous calcium carbonate suspensions in the presence of the same superplasticizer. We found that applying a magnetic field it was possible to tune the onset of this DST transition at any shear rate below the one corresponding to the absence of field. At constant imposed shear rate, the jump of stress obtained when the magnetic field reached a critical value was at least of two orders of magnitude. For instance at a constant shear rate of 13s-1 when the magnetic field was reaching 4.5kA/m the stress increased abruptly over 250kPa which corresponds to the maximum torque of our home made rheometer. The fact to be able to monitor this transition and the very large stress obtained at such low field allow us to envisage new applications of magnetorheological suspensions. On the other hand it can help to a better understanding of the DST transition. In this aim we shall compare the transition in the presence of a magnetic field with the one observed in other non magnetic suspensions and will see that the contribution of the magnetic stress to the transition is not equivalent to the one of the hydrodynamic stress because of their different angular dependence relatively to the shear gradient.

Wednesday 15:50 Grand Ball

Stress correlations in the transition region of discontinuously thickening suspension flows

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In concentrated suspensions of particles in liquids, the apparent viscosity and the normal stresses are often found to undergo an abrupt transition from a low-viscosity to a high-viscosity state. This behavior happens in a range of materials, for example dispersions of submicron spheres in organic liquids to 20-micron diameter corn starch particles in water. While the mechanism may differ for different materials, one scenario which is able to explain this type of behavior is that as the shear stress increases, a stabilizing force which maintains liquid-filled gaps between the particles transitions to one in which contact occurs and frictional interactions between the particles plays a role. This lubricated-frictional transition is explored using an established simulation approach for spherical particles in viscous liquid [1,2]. The behavior will first be shown to exhibit a shear rate- or stress-induced transition which has features of a classical phase transition. The point equivalent to a critical point is thus the point at which the variation of the shear stress (and typically also the mean particle normal stress) with respect to the shear rate becomes infinite. This point is associated with a pairing of solid fraction and friction coefficient. The temporal fluctuations and spatial correlations of the mixture stress are examined and shown to exhibit a striking change as this transition is crossed.

1. R. Mari, R. Seto, J. F. Morris & M. M. Denn "Shear thickening, frictionless and frictional rheologies in non-Brownian suspensions" J. Rheol. 2014; 2. R. Mari, R. Seto, J. F. Morris & M. M. Denn 2015 Discontinuous shear thickening in Brownian suspensions by dynamic simulation. Proc. National Acad. Sci. 112. 15326.

Wednesday 16:30 Grand Ball

How does a shear-thickening fluid flow?: Finite-size effect, non-local rheology and flow cooperatively <u>Annie COLIN</u>¹, Guillaume CHATTE¹, Guylaine DUCOURET¹, Francois LEQUEUX¹, Nadège PANTOUSTIER¹, nicolas BoQUILLON², Richard Peres², Sébastien Manneville³, Brice SaINT MICHEL³, and Guillaume Ovarlez⁴ ¹ESPCI, ESPCI, Paris, France; ²Tarkett GLD, Wiltz L-9559, Luxembourg; ³Physics Laboratory, Ecole Normale Superieure de Lyon, Lyon F 69007, France; ⁴Laboratory of Future, pessac 33600, France

Dense pastes, cement slurries or suspensions of cornstarch in water are the most common examples of shear-thickening systems. In this work, we study the flow in various geometries of two model systems . The first system is made of polyvinyl chloride (PVC) micrometric particles in 1,2-cyclohexane dicarboxylic acid di-isononyl ester (Dinch). The second system is made of PPMA particles in water and salt. For this purpose, we use state of the art velocimetry measurements and Xray tomography experiments combined to classical rheological measurements. For these two systems, the rheological behavior depends upon the confining and upon the roughness of the surfaces. Increasing the gap, decreases the shear rate at which shear thickening occurs. Increasing the roughness of the geometry, decreases the value of the measured viscosity. From Xray tomography experiments, we show that the particle concentration remains constant and homogeneous in the sample, whatever the geometry used and whatever the applied shear stress. From velocimetry measurements, we show that no slip occurs. These experiments clearly point out that non local effects occurs in those systems. To describe this behavior, a non-local theory is proposed to model dense suspension. The idea is to describe the rearrangements occurring when a dispersion is sheared as a self-activated process. A rearrangement at one position is triggered by the stress fluctuations induced by rearrangements elsewhere in the material.

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Wednesday 16:50 Grand Ball

Pairwise interparticule interactions determine discontinuous shear thickening transition in non-coloidal suspensions

<u>Jean Comtet</u>¹, Guillaume Chatté², Antoine Niguès¹, Lydéric Bocquet¹, Alessandro Siria¹, and Annie COLIN² ¹Ecole Normale Supérieure, Paris, France; ²ESPCI, ESPCI, Paris, France

The process by which non-coloidal suspensions go through a dramatic change in viscosity at a critical shear stress is known as discontinuous shear thickening. Although well-characterized on the macroscale, the microscopic mechanisms at play in this transition are still poorly understood. Using a quartz-tuning fork based Atomic Force Microscope, we characterize the pairwise force profile between two approaching PVC beads in solvent. Our set-up allows us to disentangle frictional and conservative interactions for both normal and tangential (shear-like) relative motion of the beads. We see a clear transition from (1) a low-friction regime, where the two beads support a finite normal load due to the entropic repulsion of the polymer brush while interacting purely hydrodynamically to (2) a high-friction regime characterized by hard repulsive contact between the beads and sliding friction. Critically, by continuously changing solvent properties, we show that the normal stress needed to enter the frictionnal regime at the nanoscale matches the critical stress at which shear thickening occurs in macroscopic suspensions. Our experiments thus bridge nano and macroscales, and provide long-time needed characterizations of the role of frictionnal forces in discontinuous shear thickening.

Wednesday 17:10 Grand Ball

Effect of bimodal size distribution of dense colloidal silica suspensions in PEG on reversible shear thickening

Zahra Daneshfar¹, Fatemeh Goharpey¹, Hossein Nazokdast¹, and Reza Foudazi²

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We investigated the reversible shear thickening transition of highly concentrated bimodal suspensions of silica in polyethylene glycol (PEG) with a molecular weight of 400 g/mol as a function of the volume fraction ratio of the large particles (R). It was found that the zero-shear viscosity and shear thickening behavior are non-monotonic functions of R. Sample with R=0.6 showed the lowest zero-shear viscosity and the weakest shear thickening behavior. Additionally, the empirical model for hydrocluster formation was used to discuss hydrodynamic and thermodynamic contributions to the viscosity and to determine the shear rate characterizing the onset of hydrocluster formation, PeHC. The lowest PeHC was obtained for sample with R=0.6.

Wednesday 17:30 Grand Ball

Shear thickening of non-Brownian dense suspension under confining pressure

Junhao Dong¹ and Martin Trulsson²

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We studied the discontinuous shear thickening (DST) of dense suspension using numerical simulation. DST is said to arise when there is a transition from lubrication to frictional contact between two particles. To mimic this transition, we use the Critical Load Model (CLM) for contacts between two particles. In this model, a frictional contact is defined by introducing a normal threshold force, f^{cl} . A contact is counted as frictional when the normal force between the two particles is larger than the threshold. Previous simulations using the same model have shown S-shape flow curves under constant volume fraction, φ . Here, we perform the simulation under constant confining pressure, P, and constant global shear rate, $\dot{\gamma}$, with different threshold forces. For reference, fully frictional and fully frictionless cases are used, where the contacts are always frictional or frictionless. For each threshold, viscous number, $J = \eta_0 \dot{\gamma}/P$, is varied by changing either pressure or shear rate, where η_0 is the viscosity of the background flow. We look at the viscosity-volume fraction curves, η - ϕ , for all thresholds and see crossovers between frictionless curve and frictional one in both cases. However, while the viscosity increases monotonically with volume fraction under constant f^{cl}/Pd , d being the average diameter of the particles, we observe S-shape curves under constant $f^{cl} d/\dot{\gamma}\eta_0$. The results we get in both cases fulfill the relation $\eta = k(\phi_c - \phi)^{-n}$, where f_c is the maximum volume fraction a system can reach with a given threshold force and pressure, k, f_c and n are all functions of fraction of frictional contacts, χ_f . Hence, $\eta = \eta(\phi, \chi_f)$.

Symposium NF

Non-Newtonian fluid mechanics and fluid instabilities

Organizers: Natalie Germann and Suzanne Fielding

Wednesday 13:00 Amalienborg

Dynamics of coalescent immersed jets under viscoelastic effects

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The paper investigates the elasticity influence on coalescent jets immersed in a pure viscous fluid. The study is focused on the time evolution of the meniscus which remains attached to the nozzles. In particular, the dynamics of the upper-meniscus boundary is analyzed using the Fourier decomposition, as function of the fluids rheology. In order to emphasize the elastic effects, dilute and semi-dilute polyacrylamide solutions were tested in comparison to the water-glycerin solutions. Below a certain Re number value, at a fixed distance

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between the horizontal nozzles, the meniscus interface exhibits periodic oscillations due to the downstream drop detachment. Increasing the elasticity of the injected fluid has a stabilizing effect on the meniscus, the flow dynamics between the nozzles subsequently reaching a quasi-steady state. The maximum distance between the nozzles which keeps the meniscus out of breaking was also investigated; that distance increases with the relaxation time of the polymer solution. A "taut spring" model is proposed to characterize the dynamics of the phenomena, the measured time evolution of the upper-meniscus shape being compared with the numerical solutions of the obtained equation.

Wednesday 13:20 Amalienborg

Exchange flows of viscoplastic liquids in vertical tubes

Paulo R. de Souza Mendes, Priscilla R. Varges, Mônica F. Naccache, Bruno S. Fonseca, Cunha João, and Camila Moreira Department of Mechanical Engineering, PUC-Rio, Rio de Janeiro, Rio de Janeiro 22451-900, Brazil

Well plugging for abandonment is an essential operation performed under a variety of conditions. The success of the operation is related to the capability of the cement plug to remain on the top of the drilling fluid while it sets, which can take several hours. However, gravity tends to move cement plugs downwards, due to their larger density relative to the drilling fluid underneath. The aim of the research is to better understand cement plug stability. To this end, we performed an experimental study with two immiscible liquids in a vertical tube considering viscoplastic and interfacial effects. The elasto-viscoplastic fluids are Carbopol® 980 aqueous solutions at different concentrations, and the lighter fluids are either Soya soybean oil or Shell Tellus Premium Oil 46. The influence of interfacial tension was studied through the use of surfactants. The test section consists of a Plexiglas tube, 44mm internal diameter and 660mm length, with a Mylar® sliding gate to ensure an initially flat interface. Flow visualization was performed with a digital camera, and the terminal velocities of the heavier fluid were obtained through image analysis. The influence of the governing parameters on the interface stability, front velocity at terminal motion, and morphology was investigated. Three different equilibrium regimes were observed, namely unstable, metastable, and stable (no flow). The unstable regime is a wavy core-annular flow with the denser fluid in the core that begins instantaneously after gate removal. In metastable equilibrium a plug flow develops after a delay time. For the limiting cases of unstable equilibrium regime, the presence of surfactant changes the force balance by reducing the interfacial tension contribution, thus favoring the onset of flow. It was observed that interfacial tension does not affect significantly terminal velocity. Moreover, the denser fluid velocity (zero or finite) can be estimated from the state of equilibrium analysis through dimensionless parameters.

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Flow of a second order oluid through a porous medium: Rheological validation of a generalized Darcy's equation

<u>Mario Minale</u>¹, Claudia Carotenuto¹, Liana Paduano¹, Thomas Schweizer², and Jan Vermant² ¹Dept. of Industrial and Information Engineering, Università della Campania Luigi Vanvitelli, Aversa, CE, Italy; ²Department of Materials, ETH Zurich, Zurich, Switzerland

The flow of a non-Newtonian fluid through and over a porous medium occurs in a variety of industrial, biological and environmental applications as resin transfer moulding, propagation of blood through kidney, environmental clean-up technologies, and injection of drilling fluids in rocks either for wells reinforcement or for enhancing oil recovery. Finally, important is the flow through and over a roughened geometry that is encountered in rheometry. Roughened geometries are indeed used to prevent, or reduce, the apparent wall slip often observed with, e.g., multiphase fluids and/or highly non-Newtonian fluids. A convenient way to study such problems is with homogenized equations like those of Darcy, or Brinkman, valid for Newtonian fluids. Phenomenological modifications of Darcy's law to account for the fluid non-Newtonianess are available in the literature for shear thinning fluid. Recently, Minale (2016a,b) developed a generalization of Brikman's equation for second order fluids, in the sense of Coleman and Noll, and the corresponding boundary condition to be applied at the interface between a porous medium and a homogeneous fluid. The second order fluids have a general behaviour to which each real fluid tend the limit of slow must in flows We here experimentally validate the theory proposed by Minale (2016a,b) by choosing a cross-hatched geometry as an ideal brush-like porous medium and two Boger fluids, with different elasticity, as the model fluids obeying the second order constitutive equation. We used an ARES-G2 (TA Instruments) equipped with a cross-hatched geometry on a single plate and we measured both the velocity at the interface and the first normal stress difference. We compared the experimental results with the model predictions and we validated the important theoretical results that the new non-Newtonian permeability depends on the porous medium characteristics, only.

References: Minale M., Phys. Fluids, 28, 023102, 2016a; Minale M., Phys. Fluids, 28, 023103 2016b.

Wednesday 14:00 Amalienborg

Viscoelastic Flow Simulations in Random Porous Media

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Polymer liquids are used in the oil industry to improve the volumetric sweep efficiency and displacement efficiency of the oil from a reservoir. Surprisingly, it is not only the viscosity but also the elastic properties of the displacing fluid that determine the displacement efficiency. This may be caused by the ability of a viscoelastic fluid to pull oil out of dead-ends. The aim of our work is to obtain a fundamental understanding of the effect of fluid elasticity, by developing an advanced computer simulation methodology for the flow of non-Newtonian fluids through porous media. We simulate a 3D unsteady viscoelastic flow through a model porous medium using computational fluid dynamics. The primitive variables velocity, pressure and stresses are used in the formulation. The physical and rheological properties of actual polymer solutions used in polymer flooding have been incorporated, where the viscoelastic stress part is formulated using a FENE-P type of constitutive equation. The simulations are performed using a finite volume methodology with a

staggered grid. The solid-fluid interfaces of the porous structure are modeled with a second ordered immersed boundary method. The porous medium is generated by placing stationary spherical particles of equal size in random positions using a Monte Carlo method. By means of 3D periodic boundary conditions we model the flow behavior for Newtonian and viscoelastic fluids through such a porous structure. The effect of porosity and different Deborah numbers (De) is studied in detail. The simulations provide insight on how flow structure and viscoelastic stresses change with increasing De number. To our surprise we observe completely different flow structures at high De through various pore configurations. The simulations provide a detailed understanding of the strong interplay between fluid rheology and flow topology in a random porous medium. This work has a significant importance for applications in oil recovery, polymer and food processing, and other industries.

Wednesday 15:50 Amalienborg

Making a hole in a viscoelastic film: the role of deformation history

Daniele Tammaro¹, Rossana Pasquino¹, Massimiliano M. Villone¹, Gaetano D'Avino¹, Ernesto Di Maio¹, Antonio Langella¹, Nino Grizzuti², and Pier Luca Maffettone¹

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The main feature of a viscoelastic fluid is the presence of a fading memory. As a consequence, the fluid remembers the past deformation history over times of the order of the material relaxation time. Such a feature is of particular interest when a hole is made through a liquid thin film and the subsequent hole opening dynamics are considered. For a purely viscous fluid (and if inertia can be neglected) the opening speed depends solely upon the balance between surface tension and viscous forces. On the contrary, when elasticity comes into the game, it plays a complex and relevant role. In this case, the elastic energy possibly stored in the fluid during film formation can make the initial film retraction faster (possibly much faster) than in the purely viscous case. The practical consequences of this concept are investigated in the present contribution. In particular, a home-made apparatus is used to generate a viscoelastic bubble by inflating a thin viscoelastic film. Immediately following inflation, a hot needle creates a small hole in the film, and its opening dynamics are quantitatively measured by image processing of a high-speed camera movie. The experimental results show that the initial hole opening speed increases as the film inflation rate increases, thus proving the role of the elastic energy stored during the film inflation. We also show that a simple, yet physically sound mathematical model is able to capture the essence of the observed behaviour without the need of adjustable parameters.

Wednesday 16:10 Amalienborg **Dewetting of freely suspended films of polymer solution** <u>Jiajia Zhou</u> and Masao Doi *Beihang University, Beijing, China*

We study the dewetting of freely suspended films of polymer solution, where viscous effect are dominant. This problem is interested in many industrial process such as curtain coating. We develop a one-dimensional model that takes into account the rheological properties of polymer solutions. We numerically solve the evolution equation and compare to the scaling results.

Wednesday 16:30 Amalienborg

Displacing difficult yield stress fluids from pipes

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Having yield stress fluids (YSFs) stuck in ducts is a common occurrence in industrial and natural settings that range from flow assurance in pipelines, through mucus-blocked aioli in pneumonia to the cleaning of dairy products in food processing. Here we give an overview of recent experimental studies in which pipes filled with YSFs (Carbopol) are cleaned by displacing with a Newtonian fluid (water). In these experiments we focus on regimes where the yield stress is the dominant stress in the system and hence removal is ``difficult". We explore these flows by varying rheology, flow rates, pipe inclination and density differences. Dimensionlessly we vary the Reynolds number, inclination, Atwood number, viscosity ratio and Froude number, all at very large Bingham numbers. Broadly, 3 types of displacement flow are observed: central flows, slump flows and mixed flows. The transition between central and slump flows appears to be governed by the ratio of Reynolds and Froude number (equivalent to the Archimedes number). For any flow parameters, a sufficiently large Reynolds number results in mixed displacements, i.e. via turbulence, but mixing may be instigated at lower Reynolds numbers by viscosity or buoyancy-driven instabilities. Without any buoyancy increasing the Reynolds number results in progressively smooth interfaces between fluids: low Reynolds numbers counter-intuitively lead to progressively wavy and irregular interface. In vertical displacements varying the density difference (Atwood number) from positive to negative has 2 main effects. First the overall effectiveness of the displacement front. These fingers can propagate either initially in the centre, or near the wall, often adopting helical patterns as they destabilize and mix. In between these parameters a whole zoo of interesting flow types are observed, as we review.

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Wednesday 16:50 Amalienborg Flow of gas bubbles through yield stress fluids

William L. Candela, Mônica F. Naccache, Cristiana D. Abreu, and Paulo R. de Souza Mendes

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Flow of gas bubbles through non-newtonian fluids is of great interest in several applications, including bioreactors, food processing, and drilling and cementing of oil wells. In this work we perform a study of the displacement of air bubbles in yield stress fluids. The experimental study includes the analysis of the influence of bubble size and fluid rheology on the terminal velocity displacement, and on the shape of the bubble. Elastic and thixotropic effects are discussed, as well as the effect of shear history on bubble displacement. The experimental results are obtained via flow visualization, performed in a square tank filled with the yield stress fluid. A syringe pump is used to inject the air bubble in the tank. The results are obtained for Reynolds number ranging from 10-4 to 20. The Reynolds number is defined as Re=?vtDeff/?c, where ? is the fluid density, vt is the bubble terminal velocity of the bubble are functions of buoyancy, inertia, elastic and viscous/yield stress effects. Moreover, it is observed that shear history and thixotropy have important effects on the bubble displacement. A numerical solution is also obtained for a flow of one and more bubbles through a Herschel-Bulkley fluid between parallel plates. The solution is obtained using the finite volume technique, and the volume of fluid model is employed to deal with the bi-phase (air/Herschel-Bulkley fluid) flow. The effect of fluid rheology, bubble diameter and number/position of bubbles on the velocity, pressure and strain rate fields around the bubble(s) are analyzed. In addition, a qualitative comparison with the experimental results is performed.

Wednesday 17:10 Amalienborg

Cloaking phenomena in the settling of particles in yield stress fluids

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In Stokes flow of particles in a yield stress fluid there exists a critical ratio of the body force (typically buoyancy) to the yield stress (times an area) that must be exceeded in order for a particle to move. This ratio, captured as a yield number or plastic drag coefficient, can be computed from either the mobility formulation of flow problem, or from a resistance formulation in the limit of large Bingham number. In solving such problems the focus is on the shape of the plugs attached to the particle and on the limiting yielded regions. This is important because the attached plugs effectively alter the shape of the particle and as a result significantly affect the plastic drag coefficient. A very interesting "cloaking" effect arises in this limit. The unyielded envelope (particle plus attached rigid plugs) may be identical around particles of completely different shapes, which results in the same plastic drag coefficient. Essentially, the unyielded envelope cloaks the precise shapes inside. Using the characteristic lines of a perfectly-plastic flow, we have developed a general rule that can predict the unyielded envelope around a 2D particle of arbitrary shape. Using this we may effectively approximate the yield number of the particle: the forward problem. However, the inverse problem of identifying the particle shape from the yield number cannot be solved. At most the unyielded envelope defines an effective density (of particle plus unyielded fluid), but not the particle shape. The unyielded envelope is also not defined uniquely by the yield number.

Wednesday 17:30 Amalienborg Farady's instability in yield stress fluids

Ian A. Frigaard¹ and <u>Cherif Nouar</u>²

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When a horizontal fluid layer is subjected to vertical oscillations, its free surface becomes unstable to standing waves beyond a certain threshold. Faraday's instability in Newtonian fluids has been extensively studied. The interest to Faraday's instability in complex fluids is very recent and concerns mainly viscoelastic fluids. In the case of viscoplastic fluids, i.e. fluids that exhibit a yield stress, formation of persistent holes was observed experimentally rather than Faraday waves. In the present communication, we present an analysis of Faraday's instability for a viscoplastic fluid in terms of lubrication theory. It is worthy to note here that the classical linear theory can't be used. We consider a layer of an incompressible yield stress fluid on a horizontal plate that is subjected to a vertical sinusoidal oscillation of given amplitude and angular frequency. The rheological behavior of the fluid is described by the Herschel-Bulkley model. We suppose that the initial profile of the interface fluid-air varies over a horizontal length scale, L, i.e. initially the interface is not flat. Hence, in the basic state, a horizontal pressure gradient exists in the stationary fluid layer, induced by horizontal gradients in elevation and surface curvature. We assume that the mean depth of the fluid layer is much smaller than the horizontal characteristic length. The objective is to develop a thinfilm style of model. After an appropriate scaling of all variables, the governing equations and the boundary conditions are rendered dimensionless. The leading order problem is integrated using the rheological flow. Finally, an equation relating the elevation of the interface fluid-layer to the horizontal flux of the fluid is obtained and solved numerically. Four different regimes were obtained depending on the amplitude oscillation and the Bingham number : (1) static layer, (2) weak spreading, (3) strong spreading and (4) unstable regime.

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Symposium SM

Polymer solutions and melts

Organizers: Giovanni Ianniruberto and Qian Huang

Wednesday 13:00 Christiansborg Crystallinity of polyethylene in uni-axial extensional flow

Sara L. Wingstrand¹, Martin van Drongelen¹, Kell Mortensen², Richard S. Graham³, Qian Huang¹, Bo Shen⁴, Julie A. Kornfield⁴, and Ole Hassager¹

¹Technical University of Denmark, Kgs. Lyngby, Denmark; ²University of Copenhagen, København Ø, Denmark; ³University of Nottingham, Nottingham, United Kingdom; ⁴California Institute of Technology, Pasadena, CA, United States

Flow history of polymer melts in processing greatly influences the crystallinity and hence the solid properties of the final material. A wide range of polymer processes involve extensional flows e.g. fiber spinning, blow moulding etc. However, due to instrumental difficulties, experimental studies on polymer crystallization in controlled uniaxial extension are quite rare compared to studies of crystallization in shear. Inherently uniaxial extensional flows are strong and simple relative to shear flows, in the sense that chain stretch is easily obtained and that the molecules experience no tumbling, hence much can be learned from studying polymers in extension. Recent advances in filament stretching rheometry now enable the performance of controlled uniaxial stretching of polymeric liquids even to high Hencky strains [1]. In addition the instrument allows for quenching at specific strains such that crystallization from a stretched state can take place. In this work we explore this feature in the attempt to link the nonlinear extensional rheology to the final morphology. We investigate polyethylenes (PE) of various chain architectures and observe that, even for complex architectures like long chain branched PE, the final morphology is determined by the stress at quench. This can be explained by realizing that nonlinearity in stress arises from changes in molecular configuration such as chain stretch. Hence the nonlinear stress response reflects the molecular configuration during stretching determining the final morphology [2].

[1] Román Marín, J.M. et al., J. Nonnewton. Fluid Mech. 194 , 14 (2013). [2] Graham, R.S. et al., Phys. Rev. Lett. 103 (11) , 1-4 (2009).

Wednesday 13:20 Christiansborg

Modulus increase and crystallization evolution during gel spinning and post drawing of UHMWPE fibers Nicolas J. Alvarez, Christopher Henry, and Giuseppe R. Palmese

Chemical and Biological Engineering, Drexel University, Philadelphia, PA 19104, United States

We revisit the old problem of high modulus and high strength UHMWPE fibers from gel spinning and post drawing. The goal of this work as opposed to previous investigations is to understand the structure and modulus evolution as a function of strain and stress during the evolution of the fiber during processing. Two unique apparati have been built to monitor the stress and strain evolution in the gel spinning and post drawing unit operations. The gel spinning apparatus monitors the deformation of the polymer solution as a function of time and position during extrusion from the nozzle as a function of different temperatures, strain rates, and crystallization time. The stress and strain during post drawing is monitored using a filament stretching rheometer with novel sample plates to monitor the evolution of modulus and crystallization as a function of draw ratio. SAXS and Raman measurements are used ot determing crystallization. SEM and AFM images of the fiber crystalline morphology are monitored as a function of traditional processing variables.

Wednesday 13:40 Christiansborg

Flow-induced crystallization of i-PP studied by RheoNMR and RheoSAXS

<u>Volker Räntzsch¹</u>, Mürüvvet B. Özen¹, Karl-Friedrich Ratzsch¹, Eric Stellamanns², Michael Sprung², Gisela Guthausen³, and Manfred Wilhelm¹

¹Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology - KIT, Karlsruhe, Germany; ²PETRA III, P10 Coherence Applications, German Electron Synchrotron - DESY, Hamburg, Germany; ³Institute for Biological Interfaces 4, Pro2NMR, Karlsruhe Institute of Technology - KIT, Karlsruhe, Germany

We present a study on quiescent and flow-induced crystallization of isotactic polypropylene (i-PP) using novel RheoNMR and RheoSAXS techniques. The RheoNMR set-up [1-3] is based on a strain-controlled TA ARES with an integrated TD-NMR unit (30 MHz) which provides in-situ information on microscopic molecular dynamics of polymer chains on a nanometer and micro-/ millisecond scale. With RheoSAXS [4,5] on the other hand, we gain insight into evolving structures during crystallization on a nano-/ micrometer scale. In the current set-up [6] a Thermo HAAKE MARS II was combined with the strong and brilliant x-ray source (8.4 keV, 1021 photons/[s mm² mrad² 0.1% BW]) at the German Electron Synchrotron (DESY, PETRA III, P10) to ensure a high 2D-SAXS image quality and real time monitoring of polypropylene crystallization. A short time steady-shear protocol was employed to study flow-induced crystallization, varying temperatures and flow conditions, respectively. By the use of combined techniques we were able to determine correlations of flow behavior with the evolving crystallize attraction of oriented crystallites.

[1] Räntzsch, V.; Wilhelm, M.; Guthausen, G. Magn. Reson. Chem. 2016, 54(6), 494-501.

[2] Özen, M. B.; Räntzsch, V.; Ratzsch, K.-F.; Guthausen, G.; Wilhelm, M. Ann. Trans. Nordic Soc. 2016, 24, 33-39.

[3] Ratzsch, K.-F.; Friedrich, C.; Wilhelm, M. J. Rheol. 2016 (submitted).

[5] Meins, T.; Hyun, K.; Dingenouts, N.; Ardakani, M.; Struth, B.; Wilhelm, M. Macromolecules 2012, 45, 455-472.

[6] Stellamanns, E.; Meissner, D.; Lohmann, M.; Struth, B. J. Phys. Conf. Ser. 2013 425(20), 1-3.

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SM25

^[4] Struth, B.; Hyun, K.; Kats, E.; Meins, T.; Walther, M.; Wilhelm, M., Grübel, G. Langmuir 2011, 27(6), 2880-2887.

Wednesday 14:00 Christiansborg

Hyphenation of Rheology and Raman Spectroscopy - Investigation of epoxy curing mechanism and polyethylene crystallization

Michael Kempf, Bernd Dippel, and Oliver Arnolds

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Hyphenation of a rheometer and a Raman spectrometer enables a correlation between molecular structure (Raman) and macroscopic mechanical (Rheology) properties at the same time. The hyphanation of these two techniques allows us not only to better understand the underlying curing processes but also to study crystallization of polymers.

The instrumental setup that we have developed uses a rheometer (MCR 302 from Anton Paar, Austria) that has been coupled via a fiber optic Raman probe with a Raman Spectrometer (UHTS 300 from WITec, Germany). Measurements can be performed in a temperature range which varies between -40 and +200 °C. Raman spectra are excited using a 532 nm laser and covers a spectral range from 200-3900 cm-1. The hyphenation of a rheometer and a Raman spectrometer has already been refered to in the literature [1-5].

The current instrumental setup offers an advantage over the existing methods by allowing disposable parallel plate geometries to be used thus enabling a faster turn-around of sample measurement. This advantage makes the set-up very attractive to an industrial environment.

In this study, the curing reaction of an epoxy (Epikote 828 from Hexion Specialty Chemicals, Germany) and amine (Baxxodur EC 130, Trioxatridecandiamine from BASF, Germany) system as well as the crystallization of LDPE (LDPE 1840 from LyondellBasell) were investigated.

[1] Chai, C.K. et al., Polymer 36 (1995) 661-663

[2] Farquharson, S. et al, SPIE Conference 3535 (1998) 303-316

[3] Farquharson, S. et al., Journal of Process Analytical Chemistry 7 (2001) 45-53

[4] Chevrel, MC. et al., Ind. Eng. Chem. Res. 51 (2012) 16151-16156

[5] Brun, N. et al., J. Raman Spectrosc. 44 (2013) 909-915

15:50 Christiansborg Wednesday

Shear and extensional rheology of LDPE after high-temperature extrusion

Jaap Den Doelder¹, Sylvie Vervoort¹, Armin Baserga-Jurczok², Eva-Maria Kupsch², and Bernard Fehr²

¹Performance Plastics R&D, Dow Benelux B.V., Terneuzen, The Netherlands; ²Dow Europe GmbH, Horgen, Switzerland

Polymers of the low-density polyethylene (LDPE) type are used extensively in industrial practice for their excellent shear and extensional rheology. During high-temperature processing, the rheology is not only affected by the intrinsic temperature dependence as typically described through Arrhenius shift factors, but there are indications that chemical modification also plays a role. We present systematic data on virgin and processed LDPE. Two materials with significantly different branching topology are studied. It will be shown that the rheology modification during processing is a function of specific extrusion conditions, but also of the starting polymer microstructure.

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Wednesday 16:10 Christiansborg

Derivation of a recently proposed CCR model through the use of non-equilibrium thermodynamics

Ioanna C. Tsimouri¹, Christos K. Georgantopoulos¹, Pavlos S. Stephanou², and Vlasis G. Mavrantzas³

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By default, convective constraint release (CCR) implies a variable entanglement density, since entanglements are continuously destroyed and regenerated under an applied flow (even at moderate shear rates). In particular, atomistic non-equilibrium molecular dynamics (NEMD) simulations of entangled polyethylene melts provide direct evidence for a decrease in the average number of entanglements per chain in the melt with increasing shear rate. Motivated by this, Marrucci and Ianniruberto [Philos. Trans. R. Soc. London A 2003, 361, 677-688] proposed a new version of the CCR theory by considering (in addition to the evolution equation for tube orientation and chain stretch) an extra equation for the (scaled) entanglement density. In the present work we revisit a recently proposed constitutive model for the rheological description of entangled polymer melts developed in the context of nonequilibrium thermodynamics [P.S. Stephanou, I.Ch. Tsimouri, V.G. Mavrantzas, Macromolecules 2016, 49, 3161-3173] by allowing for a variable entanglement density due to applied flow. To this, we have added the entanglement density in the vector of state variables and have properly redefined the Poisson and dissipation brackets, as well as the expression for the free energy of the melt. We anticipate the new constitutive model to be able to describe rheological data for the flow behaviour of entangled polymer melts using a smaller value of the CCR parameter than the model with a constant entanglement density. Using the new model to describe available rheological data is part of ongoing research work.

Wednesday 16:30 Christiansborg

Dilution of model comb polystyrenes using entangled linear side chains

Mahdi Abbasi, Lorenz Faust, and Manfred Wilhelm

Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology - KIT, Karlsruhe, Germany

Linear and extensional rheology of a series of model comb polystyrenes (comb-PS) as well as their diluted melts with entangled linear side chains was investigated. All of comb-PS had the same entangled backbone Mw,bb = 290 kg/mol and similar branches, Mw,br = 44 kg/mol,

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but varied in the number of branches per molecule, Nbr, from about 2 to 80 branches, which cover a wide range of branched structures from sparsely to highly and bottlebrush-like structure. Sparsely branched architectures had higher zero-shear viscosity than their linear counterparts, while by increasing of branches towards the highly branched structure zero-shear viscosity decreased below the linear analogues, so that the zero-shear viscosity of a comb-PS with 0.5 entanglement between the branch-point was similar to the value of its linear backbone. Increasing the branches towards the bottlebrush-like architectures drastically raised up the zero-shear viscosity due to the intermolecular interactions between the neighbour side chains. Comb-PS with 80 branches per molecule was diluted with a linear PS similar to its side chains to investigate the difference between the dilution effect of grafted side chains and free linear side chains. Extensional properties of these diluted model systems were also investigated.

Wednesday 16:50 Christiansborg

Linear and nonlinear rheology of comb/linear blends

Zhi-Chao Yan¹, Frank Snijkers², and Dimitris Vlassopoulos³ ¹Shenzhen University, Shenzhen, China; ²CNRS, Solvay UMR 5268, Laboratoire Polymères et Matériaux, Saint-Fons, France; ³Materials science and technology- University of Crete, Foundation for research and technology-Crete, Heraklion, Greece

Comb polymers, with a structure having a backbone grafted by branches, relax stress hierarchically, namely, the outer branches relax first via arm retraction and then the inner backbone relax in a solution environment with relaxed branches as solvents.[1, 2] Their nonlinear shear and extensional deformation is also examined and exhibits systematic dependence on their branching structures.[3, 4] Here, we extend our work to comb/linear mixtures and examine the role of dynamic dilution and the interplay between comb and linear matrix on both linear (LVE) and especially nonlinear (NLVE) shear viscoelasticity. Regarding LVE, different-Mw linear matrix relax either faster or slower than the branches. In the former case, linear chains and branches relax simultaneously and then trigger the backbone relaxation. Both linear chains and branches act as solvent for backbones. In the latter case, branches relax faster than linear chains so that the backbone is triggered before complete relaxation of the linear matrix. The dynamic tube dilution mechanism gradually fails. Regarding NLVE, blends exhibits double stress overshoot during shear flow as in pure comb polymers with entangled branches.[5] However, the strain where the backbone overshoot occurs is larger in blends than in pure combs. It is attributed to the tube dilation caused by forced disentanglement between backbones and linear matrix under high shear rate.

1.Daniels, D.; McLeish, T.; Crosby, B.; Young, R.; Fernyhough, C. Macromolecules 2001, 34, (20), 7025-7033. 2.Kapnistos, M.; Vlassopoulos, D.; Roovers, J.; Leal, L. Macromolecules 2005, 38, (18), 7852-7862. 3.Lentzakis, H.; Vlassopoulos, D.; Read, D. J.; Lee, H.; Chang, T.; Driva, P.; Hadjichristidis, N. J. Rheol. 2013, 57, (2), 605-625. 4. Snijkers, F.; Vlassopoulos, D.; Lee, H.; Yang, J.; Chang, T.; Driva, P.; Hadjichristidis, N. J. Rheol. 2013, 57, (4), 1079-1100. 5. Snijkers, F.; Vlassopoulos, D.; Ianniruberto, G.; Marrucci, G.; Lee, H.; Yang, J.; Chang, T. ACS Macro Lett. 2013, 2, (7), 601-604.

Wednesday 17:10 Christiansborg

Rheological and molecular characterization of long-chain branched poly(ethylene terephthalate)

Matthias Kruse, Peng Wang, and Manfred H. Wagner

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Reactive extrusion with pyromellitic dianhydride (PMDA) and epoxy-based tetraglycidyl diamino diphenyl methane (TGDDM) was conducted to create long-chain branched poly(ethylene terephthalate) (LCB-PET) starting from three different linear grades of PET. The mechanical and molecular properties were analyzed by linear and non-linear viscoelastic rheology in the melt state, as well as sizeexclusion chromatography with light scattering measurements. The two tetra-functional chain extender led to strong viscosity increases, increasing strain hardening in elongational flow, and increasing long-chain branching with increasing chain extender concentration as confirmed by loss- and storage modulus, phase angle, activation energy of flow, and elongational viscosity. The Molecular Stress Function (MSF) model predictions show good agreement with data measured, and allow a quantitative analysis of the branching structure and of the stretch of the molecules. The molecular analysis by SEC triple detection of a high molar mass PET reacted with PMDA and TGDDM shows a strong increase of the average molar masses, polydispersity, radius of gyration, and hydrodynamic radius, and confirms the molar mass increase observed by the rheological measurements. The branching was confirmed by a decreasing Mark-Houwink exponent with increasing chain extender concentration. Further, the analysis of the contraction of the molecule revealed a more star-like structure at low concentrations for both chain extenders. With increasing concentration, the structure changed to more comb-like structure for PMDA and a random tree-like or hyperbranched structure for TGDDM as was also observed by non-linear viscoelastic measurements. PMDA revealed to be an excellent coupling agent, inducing reproducibly either a star-like, comb-like, or tree-like structures depending on the concentration of the coupling agent.

Wednesday 17:30 Christiansborg

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Molecular architecture modifications for tuning melt flow properties of aliphatic pentadecalactone polyesters

Gijs de Kort¹, <u>Dietmar Auhl¹</u>, Mark Pepels², and Rob Duchateau³

¹Aachen-Maastricht Institute for Biobased Materials, Maastricht University, Geleen, The Netherlands; ²Department of Chemical Engineering and Chemistry, Eindhoven University of Technology, Eindhoven, The Netherlands; ³SABIC T&I, SABIC Europe B.V.,, Geleen, The Netherlands

Linear aliphatic polyesters like poly-pentadecalactones (PPDL) can be potentially biobased materials and also alternatives to current commodity polyolefins. Yet, the melt flow behavior of such polymer materials needs to be well designed regarding molecular structure and processability for corresponding applications, too [1].

In this study the synthesis, solution and melt characterization of several series of linear and long-chain branched PPDL are discussed in order to highlight routes towards successful modifications of polymer architecture and processing behavior as examples for the class of

biopolyesters. By correlating several model synthesis pathways and resulting molar-mass distributions as well as branching structures with melt flow behavior, significant insights have been gained for both linear and branched PPDL from a simple, one-pot synthesis of PPDL with various chain architectures.

In order to investigate and distinguish the obtained branching structures various shear and elongational rheological techniques and indicators have been used, i.e. strain-hardening and thermo-rheological behavior as well as molar-mass dependence of zero-shear viscosity and compliance. The zero-shear viscosities of star-shaped PPDL with arm lengths higher than several entanglement numbers as well as with high numbers of branches per molecule surpass that of linear counterparts. For these branched PPDL a thermo-rheological complexity is found, while strain hardening in uniaxial elongation occurs only for PPDL with high branching numbers, which can be explained by molecular structures and models with branch-on-branch architecture. The observations on the correlations between molecular structure and melt flow behavior are in good agreement with earlier findings on polyolefins [2,3].

[1] de Geus et al. Polym. Chem. (2010) 1, 525-533

[2] Wood-Adams et al. Macromol. (2001) 33, 7489-7499

[3] Auhl et al. Macromol. (2004) 37, 9465-9472

Symposium FB

Food and biorheology

Organizers: Henrik Kragh and Ulf Andersen

Wednesday 13:00 Fredensborg

FB24

Biomechanics of corneal cells quantified for the development of enhanced contact lenses Juho Pokki, Maria Merola, Emily C. Hollenbeck, Namita Nabar, Camila de Paula, and Gerald G. Fuller Department of chemical engineering, Stanford university, Stanford, CA 94305, United States

Biomechanical interactions with materials, such as contact lenses, are determined by the interfacing tissue and its contacts with the materials. Further, tissue biomechanics relate to physical conditions, and its alterations reflect changes within tissue constituents. How the corneal cells interact with contact lenses under use-related mechanical and biological conditions is not well understood. Previously, localized biomechanical properties of intracellular and extracellular environments have been investigated using multiple techniques, including atomic force microscopy (AFM) and micropipette aspiration. In order to characterize layers of controlled amounts of corneal cells, we propose a method using a live-cell monolayer rheometer (LCMR). This multi-cell method allows for the acquisition of sufficient statistics to overcome biological variation between individual cells. Further, the LCMR enables characterization of the interactions of cell layers with other biologically active layers, such as cells, extracellular constituents, or artificial surfaces (i.e. contact lenses). In this work, the LCMR was utilized to characterize corneal cell mechanics. Two different corneal epithelial models were employed: a corneal cell monolayer, and a multi-layered corneal tissue. To simulate physiological conditions during the use of contact lenses, measurements of tangential shear stresses were used. Step-strain tests with strain sweeps were carried out to quantify the mechanical relaxation of the corneal epithelial models. The relaxation data relates to intracellular rearrangements and cell-cell interactions. Furthermore, creep compliance measurements were performed to complement the data. The presented methods for quantification of corneal cell biomechanics not only facilitate the development of enhanced contact lenses, but have the potential for developing better treatments of dry-eye symptoms, as well as preventing corneal wounds and infections.

Wednesday 13:20 Fredensborg

FB25

On the relationship between rheology, microstructure and nanoparticle penetration of pulmonary mucus Christian Wagner

Physics, Saarland University, Saarbruecken, Germany

Respiratory mucus is found in the conducting airways covering the ciliated epithelium. The mucus is typically split into two layers, the periciliary layer between the cilia and the top layer forming a viscoelastic gel. The mucus layer protects the epithelium from inhaled particles and foreign materials due to its sticky nature. Accumulation of these materials is avoided as a result of the coordinated beating of the cilia the so-called mucociliary clearance. The mucus together with the mucociliary escalator of the conduction airways is a very efficient clearance mechanism also preventing efficient drug delivery across this barrier. This respiratory mucus, composed from mucin macromolecules, carbohydrates, proteins, and sulphate bound to oligosaccharide side chains forms a biological gel with unique properties. The interaction of all kind of inhaled drugs and drug carriers with this layer and the penetration potential in and through the mucus is of outmost importance for possible therapeutic approaches.

Wednesday 13:40 Fredensborg

Risk-based and Patient-centric approach to pharmaceutical product development: Rheology as a Critical **Ouality Attribute**

Andrea Sekulovic¹, Johanna Aho², Jukka Rantanen³, Thomas Rades⁴, and Ruud Verrijk⁵

¹Department of Pharmacy, University of Copenhagen, Copenhagen, Denmark; ²University of Copenhagen, Copenhagen, Denmark; ³Department of Pharmacy, University of Copenhagen, Copenhagen, Denmark; ⁴Pharmacy, University of Copenhagen, Copenhagen, Denmark; ⁵Research and Development, Dr Reddys Laboratories Ltd. IPDO Leiden, Leiden, The Netherlands

The ultimate end goal of product development is to meet the patient needs, both in terms of therapeutic criteria and patient compliance. The proposed risk-based and patient-centric roadmap helps the pharmaceutical scientist to focus the scientific research efforts on the critical quality attributes (CQA's). In this study, rheological behavior was identified as a CQA for an ocular dosage form in both qualitative and quantitative risk assessment methods. Utilized roadmap for the formulation and process development focused on the rheological properties of a complex ocular formulation as being of the utmost importance for the quality product target profile. Verification of rheological behavior in terms of the viscosity, yield stress, sol-gel transition and thixotropy is designed to the desired ocular product performance. The rheological behavior is explained applying scientific understanding of the raw material characteristics, the manufacturing process and in vivo behavior. Patient needs are met with the tailored rheological product characteristics for production, transport, storage and use of the final product. Rheology as a CQA is an indicator of an optimal product performance and hereby leads to a product that meets the patient needs.

Symposium IR

Interfacial rheology

Organizers: Natalie Medlicott and Peter Fischer

15:50 Fredensborg Wednesday

Asphaltene Adsorption: Delayed Coalescence of Water-in-Oil Emulsions and Spontaneous Droplet Formation

<u>Gerald G. Fuller</u>¹, Simone Bochner¹, Maria Merola¹, and Dimitris Vlassopoulos² ¹Chemical Engineerig, Stanford University, Stanford, CA 94305, United States; ²Materials science and technology-

University of Crete, Foundation for research and technology-Crete, Heraklion, Greece

Asphaltenes are higher molecular weight components of heavy oils characterized by marginal solubility. These aromatic compounds are polar and have a propensity to adsorb onto oil/water interfaces, rendering them viscoelastic. The resulting non-linear interfacial rheology toughens the interfaces and can delay and inhibit coalescence of water droplets within the oil, making removal of water more challenging. This paper presents work using a newly developed instrument, the Dynamic Fluid Interferometer (DFI), that allows one to follow drainage and coalescence dynamics. It is reported that coalescence times are strongly lengthened as asphaltene concentration and interfacial aging times are increased. However, a maximum is observed in the coalescence time as a function of aging times and we attribute this unanticipated behavior to a newly discovered spontaneous emulsification at the oil/water interfaces when asphaltenes are present. Using a combination of fluorescence and confocal microscopy, it is determined that these droplets, which are on the order of 50 to 100 nm, as comprised of highly concentrated asphaltene-in-oil droplets. It is conjectured that these nano-droplets serve as de-emulsifiers when present at high concentrations.

16:10 Fredensborg Wednesday

Interfacial rheology of soft microcapsules

Clement de Loubens¹, Kaili Xie², Deniz Z. Gunes³, Julien Deschamps⁴, Gwen Boedec⁴, Marc Jaeger², and Marc Leonetti⁴ ¹Université Grenoble Alpes, CNRS, LRP, Gières 38610, France; ²Aix-Marseille Université, CNRS, Centrale Marseille, M2P2, Marseille, France; ³Nestlé Research Center, Lausanne, Switzerland; ⁴Aix-Marseille Université, CNRS, Centrale Marseille, IRPHE, Marseille, France

A capsule is a drop bounded by a thin solid membrane providing specific mechanical properties. It is used to control the spatio-temporal delivery of substances in numerous processes. Its dynamics under flow depends on its membrane characteristics. Moreover, the delivery of encapsulated drugs is controlled by its deformation. The mechanical properties of microcapsules can be tuned according to their formulation. We will focus on cross-linked membranes made with human serum albumin and chitosan assembled with a surfactant via electrostatic interactions. The interfacial rheological properties of these soft microparticles are deduced from their dynamics of deformation in elongation and shear flows. In elongational flow, the surface shear modulus of the membrane is measured and related to the kind of biopolymer used and to the main parameters of the process of fabrication. In the regime of large deformations, the microcapsules can present a non-linear elastic response or plastic deformations. Non-linear elastic constitutive law is deduced by comparison of the evolution of the shape of the microcapsule in the two main planes of deformation of the capsule with numerical simulations. In shear flow, the rotation of the membrane, i.e. the tank-treading, is visualised and quantified by decorating the membrane of microcapsules with particles. The tracking of the distance between two close microparticles showed membrane contraction at the tips and stretching on the sides. This dynamics of deformation induce viscous dissipation inside the membrane. The order of magnitude of membrane viscosity is determined by comparison with numerical simulations. We will conclude the talk by some examples of breakdown of microcapsules in elongational flow.

IR2

IR1

References: de Loubens et al. , 2014, Soft Matter, 10:25, 4561-4568 / de Loubens et al. , 2015, J. Fluid. Mech., 767, R3 / de Loubens et al. , 2016, J. Fluid. Mech., 789, 750-767

Wednesday 16:30 Fredensborg

Spreading of complex fluid drops

Loren Jørgensen¹ and Catherine Barentin²

¹Aix-Marseille Univ, CNRS, IUSTI UMR 7343, Marseille 13453, France; ²Institut Lumière Matière, Univ Lyon, Université Claude Bernard Lyon 1, CNRS, Villeurbanne 69622, France

This work is a part of a broader study dealing with wetting of complex fluids. Here we describe experimentally the spreading of drops of complex fluids on a rigid wetting surface, with zero velocity at contact. We explore the effect of the rheological exponent and of the yield stress. We observe mainly two regimes, the first one at short timescales (t<10ms) and the second one at long timescales (of the order of a few minutes).

In particular, we show that in the presence of gravity, short time spreading is rapidly governed by a balance of the potential energy variation with viscous dissipation, rather than by the usual inertial description [1]. The difference between these descriptions is not visible for Newtonian fluids, but is clear for shear-thinning fluids. The power law exponent of R(t) is indeed related to the rheological exponent of the fluid.

At long times, the spreading of shear-thinning fluids is already known experimentally and theoretically [2,3]. However the case of yieldstress fluids has been addressed only recently [4]. As the shear rate vanishes, at the end of the spreading, the yield stress becomes predominant. This causes a dynamical arrest of the liquid drop, therefore the equilibrium Young's state cannot be reached. We also propose a scaling model in agreement with our observations.

[1] Biance et al, PRE, 2004; [2] Rafaï et al, JFM, 2004; [3] Starov et al, J Coll Interf Sci, 2003; [4] German & Bertola, Coll Surf A, 2010.

Wednesday 16:50 Fredensborg

Chickpea protein-stabilized emulsions: from interfacial to bulk rheology

Nadia C. Isaurralde, Manuel Felix, Alberto Romero, and Antonio Guerrero

Chemical Engineering, Universidad de Sevilla, Sevilla, Spain

Proteins are highly efficient in producing and stabilizing emulsions, by reducing interfacial tension that facilitates the breakup of oil droplets and by forming viscoelastic interfacial films that helps to stabilize oil droplets. Thus, the dynamics of complex interfaces is generally dominated by interfacial rheology, which plays a key role to prevent destabilization. Dilatational rheology is considered to be more relevant for short-term stability whereas interfacial shear is valuable for middle or long-term stability. Both viscoelastic responses often affect emulsion stability and bulk rheology. Although not yet extensively investigated, the links between interfacial properties and bulk emulsion rheology seems to be highly promising. The objective of this work is to evaluate the relationship between interfacial and bulk rheology of O/W chickpea protein-based emulsions and their contribution to emulsion microstructure and stability, as a function of chickpea protein (CPP) concentration and pH. Interfacial tension was measured as a function of time with a Wilhelmy plate fitted to a D502 tensiometer (Sigma). Interfacial SAOS rheology was studied by means of a double wall-ring geometry fitted to a DHR3 rheometer (TA Intruments). Dilatational rheology was measured using a pendant drop tensiometer (IT Concept). Emulsions were prepared using a highpressure homogenizer EmulsiFlex-C5 (Avestin). SAOS tests of emulsions were carried out with plate-plate geometry with the DHR3. Droplet size distribution was determined with a Mastersizer X (Malvern) and CLSM was performed with a LSM Duo (Zeiss). Backscattered light measurements were carried out with a Turbiscan (L'Union) to study the destabilization mechanisms of emulsions. These results confirm the relevance of performing both interfacial tension and viscoelastic measurements to select optimal conditions for emulsification. In addition, results generally show a good agreement between interfacial (shear) rheology, emulsion rheology, microstructural parameters and stability.

Wednesday 17:10 Fredensborg

Effects of nanoparticles localized at the interface on single droplet dynamics in shear flow

Helene Van Ammel¹, Yuan Mei¹, Ruth Cardinaels², and Paula Moldenaers¹

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Various daily life materials consist of immiscible polymer blends with a droplet-matrix morphology. During processing, these polymer blends are exposed to complex flow fields. The interplay between droplet deformation, retraction, breakup and coalescence in these flow fields determines the blend morphology and hence, the final product properties. To introduce an additional functionality such as conductivity or to manipulate the blend morphology, nanoparticles are often added to polymer blends. Nanoparticles which are located at the interface can control and stabilize the blend morphology by substantially suppressing coalescence. However, a fundamental understanding of the mechanisms by which nanoparticles affect structure development is still lacking. Therefore, the goal of this research is to study the impact of nanoparticles localized at the interface on single droplet dynamics, in particular on droplet deformation and breakup. A model system consisting of a Newtonian PDMS droplet in a Newtonian PIB matrix is studied in a counter-rotating shear cell combined with an optical microscope. Hydrophobic fumed silica particles with an aggregate radius of 100 nm localize at the PDMS-PIB interface, as shown by SEM images. At high particle coverages, an elastic network is formed which substantially suppresses droplet deformation and stabilizes the droplet against breakup. The droplet breakup mechanism is, however, completely different from that of a neat droplet, resulting in irregular droplet shapes. The formation of an interfacial particle network also causes hysteresis effects in the droplet deformation. These findings clearly show the importance of the interfacial viscoelastic properties. Therefore, the droplet dynamics and the relation to the interfacial viscoelastic properties is further investigated by studying the effect of particle size and particle shape.

IR3

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IR5

Wednesday 17:30 Fredensborg

Self-propelling microcapsules swimming at the surface of water: Synthesis, flow properties, swarming behavior and the analysis of the swimming motion

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Microcapsules have many applications in science and industry. Thin, flexible membranes surround these particles, so that active substances, as for instance drugs, can be stored in the core of these capsules. Special ingredients can also be incorporated as energy source for the propulsion of these capsules. We used this simple approach in order to study biological propulsion mechanisms and to transport encapsulated cargos to desired places. In a series of experiments, we investigated the swimming motions of mushroom-like microcapsules in the vicinity of the water surface. The chemical reaction between potassium permanganate, which was stored in the stem of these particles, and the fuel hydrogen peroxide, which diffused form the surrounding water solution into the capsules, leaded to the production of tiny oxygen bubbles. The release of the bubbles induced the backstroke principle, which pushed the swimmers forward. The anisometric particles moved with an average speed of 1-2 cm/s for a period of at least 10-20 minutes. In a series of experiments, we analyzed many details of the swimming motions such as the velocity fluctuations, the inclination angles, the trajectories, collisions and the behavior of these particles in the vicinity of the walls. In additional investigations, we examined lens-like alginate capsules. Polyethylene glycol (PEG) or other liquids, which were stored in the core of these particles, could be released through small pores of the membranes. Due to the spreading process of these liquids, the alginate capsules showed rapid, circular motions. We investigated these movements by optical tracking analysis of positions and speeds. After addition of surfactants, we observed more complicated collective swimming processes, and the capsules formed then well-ordered structures like pulsating rings or oscillating chains.

Symposium PG

Rheology of powders and granular material

Organizers: Changquan Calvin Sun and Dietmar Schulze

Wednesday 13:00 Kronborg

Suppression of the threshold of a granular solid by mechanical fluctuations

Adeline Pons¹, Jerome Crassous², Eric Clement¹, and <u>Axelle Amon²</u>

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For a granular material, when the ratio between the shear stress and the confining pressure is smaller than the Mohr-Coulomb threshold, the system can be considered as a solid. Nevertheless, a long-term creep is observed in this solid phase in stress imposed experiments. This creep process is the result of the accumulation of localized plastic events and can be interpreted using a generic rheological model. We present recent experimental and theoretical results demonstrating that the superposition of tiny regular oscillations to the imposed stress are sufficient to change the response of the system from a logarithmic creep to a linear one even deep in the jammed phase. We give a theoretical interpretation of this fluidization without invoking an effective temperature due to a mechanical noise. Indeed, as the perturbation we imposed is regular, it cannot be modeled by a noisy term. We interpret our observations as a ratcheting process which is revealed only on very long time. We use a method of measurement of minute deformation based on Diffusing Wave Spectroscopy to study the spatial repartition of the deformation in the material for the two regimes of creep observed (logarithmic and linear). We show that the model developed to describe the macroscopic measures is in agreement with the spatially-resolved measurements.

Wednesday 13:20 Kronborg

Power Law Behavior in Rheology of Granular Matter

<u>Thomas Petersen</u>, Maria B. Larsen, Mia F. Falkeborg, Eleonora M. Becker, and Anne L. Nielsen *Food Technology, Danish Technological Institute, Aarhus C 8000, Denmark*

The flow of powder is a complex topic, which has garnered attention from researchers in the past, but much of the behavior remains poorly understood and the coupling to industrial applications is only mastered for silo design. Depending on a long range of particle characteristics and external factors powder may exhibit many different types of behavior with analogues in solid, liquid and vapor physics. In this work, we attempt to take steps at understanding powder flow generally, in order to shorten the gap between laboratory measurements and industrial application.

We have used a powder rheometer similar to a Couette-system, with a stationary outer wall and a moving, profiled inner wall. The inner wall is profiled to ensure a non-slip boundary condition. The rheometer is developed by Anton Paar and allows for the derivation of a powder viscosity using equations known from traditional rheology. The rheometer also allows partial or full fluidization by sending an air current through the powder at controlled rates, thus making different degrees of packing or compactivity accessible. The combination of varying compactivity and shear rate allows for measurements of powder behavior in a large range of conditions.

We report the results of measurements for different powders with varying flow rate of air through the sample and with varying shear rate. The viscosity of the granular materials tested show shear-rate dependence similar to that of a power law fluid. Some samples even showed plateaus at low or high shear, fitted well with the Carreau-Yasuda equation. The dependency upon the flow rate of air appears similar to how a fluid changes viscosity with temperature. Given these similarities to fluid rheology the results will be interpreted as such, with analogues between powder compactivity and fluid temperature as suggested by past theoretical work.

PG1

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Wednesday 13:40 Kronborg Frictional rheology of wet granular matter

Stefan J. Gstöhl, Lukas Schlumpf, Peter Fischer, and Erich J. Windhab

Institute of Food, Nutrition and Health, ETH Zurich, Zurich, Switzerland

For numerous application such as in geotechnics, building materials science, or process engineering, wet granular matter is of common interest. However, a wide spectrum of material properties complicates the rheological characterisation of such materials. Frictional rheology describes successfully dry granular flow and suspension rheology by introducing a friction coefficient and a dimensionless inertial or viscous number, which is solely a function of the volume fraction [1]. Wet granular matter defines the state in between dry and suspension state. However, this regime has not been studied yet experimentally under the same framework. In this contribution we present an experimental study of wet granular material. A normal force controlled ring shear cell was used to study the frictional rheology of wet granular material at high volume fractions considering different water contents and particle sizes. In addition to the volume fraction, liquid saturation or capillary forces determine the frictional rheology of wet granular matter. Incipient flow measurements, characterizing the yield stress and the static friction coefficient, demonstrate that capillary forces cause a strong increase in yield stress and friction coefficient, whereas slow steady state flow is characterised mainly by the particle contact contribution and can be observed for dense suspensions at low shear rates as well. Our approach provides an experimental access towards the implementation of capillary forces in the framework of frictional rheology and could potentially bridge the gap between dry granular flow and suspensions rheology.

[1] F. Boyer, É. Guazzelli, and O. Pouliquen, Phys. Rev. Lett. 107, 188301 (2011)

Wednesday 14:00 Kronborg

Steady-State Friction Measurements of Granular Materials Under Pressure Using GFA apparatus Marko Bek¹, Joamin Gonzalez-Gutierrez², and Igor Emri³

¹Center for Experimental Mechanics, Faculty of Mechanical Enginering, University of Ljubljana, Ljubljana, Slovenia; ²Montanuniversität Leoben, Leoben, Austria; ³Center for Experimental Mechanics, Faculty of Mechanical Enginering, University of Ljubljana, Ljubljana, Slovenia

Flow of granular material during processing, handling and transportation strongly influences the quality of the final product and its cost, that is why it is important to measure flow properties of granular materials. Flowability of granular materials depends on the characteristics of the material and on the conditions at which flow is occurring. In this paper a new methodology is introduced to measure friction between granular materials under pressure induced with uniaxial compression. Apparatus also allows analysis of conditions at which granular material starts to flow when exposed to uniaxial compressive load, i.e., zero-rate flowability. We call the apparatus the Granular Friction Analyzer (GFA). The concept of the GFA was tested by measuring four different materials with different average particle sizes. It was observed that as the particle size decreases so does its zero-rate flowability. This is in agreement with powder literature. Therefore, it can be concluded that in general the GFA method can be a very useful tool to study friction between granular materials and conditions at which the granular material flow initiates, i.e. zero-rate flowability of powders under pressure.

Wednesday 15:50 Kronborg

Dry granular flows: rheological measurements of the \mu\left(I\right)-rheology

<u>Abdoulaye FALL¹</u>, Michel BADETTI², Jean-Noël ROUX³, and François CHEVOIR⁴ ¹Laboratoire NAVIER, Champs sur Marne 77420, France; ²Laboratoire NAVIER, Champs sur Marne 77420, France; ³Laboratoire NAVIER, Champs sur Marne 77420, France; ⁴Laboratoire NAVIER, ⁴Laboratoire NAVIER, ⁴Laboratoire NAVIER, ⁴Laboratoire NAVIER,

Granular materials do not always flow homogeneously like fluids when submitted to external stress, but often form rigid regions that are separated by narrow shear bands where the material yields and flows. This shear localization impacts their apparent rheology, which makes it difficult to infer a constitutive behaviour from conventional rheometric measurements. Moreover, they present a dilatant behaviour, which makes their study in classical fixed-volume geometries difficult. These features led numerous groups to perform extensive studies with inclined plane flows, which were of crucial importance for the development and the validation of the \mu\left(I\right)-rheology. Our aim is to develop a method to characterize granular materials with rheometrical tools. Using rheometry measurements in an annular shear cell, dense granular flows of 0.5 mm spherical and monodisperse beads are studied. A focus is placed on the comparison between the present results and the \mu\left(I\right)-rheology. From steady state measurements of the torque and the gap under imposed shear rate and normal force, we define an inertial number I . We show that, at low I, the flow goes to a quasi-static limit, and the response in terms of dimensionless stress or internal friction coefficient -\mu- and solid concentration - \phi - profiles is independent of the inertial number. Upon increasing I, dilation occurs and \phi decreases while \mu increases. The observed variations are in good agreement with previous observations of the literature (Jop et al. 2006; Hatano 2007). These results show that the constitutive equations \mu\left(I\right) and \phi)left(I\right) of granular materials can be measured with a rheometer.

Wednesday 16:10 Kronborg Granular rheology of ellipses

Martin Trulsson

Department of Chemistry, Division of Theoretical Chemistry, Lund University, Lund, Sweden

We study the granular rheology of dense amorphous assemblies of ellipses in steady flow by numerical simulations. The simulations are carried out in a planar shear cell under various confining pressures P, constant shear rates γ , and aspect ratios of the ellipses principal axes α . Following similar studies for disks/spheres we define the inertial number as I ~ γ /P. Constitutive relations for the steady flows are given as function of this inertial number at different aspect ratios for both frictionless and frictional assemblies. Well-defined mechanical stable packings are generated by slowly decreasing the inertial number to zero. Both frictional and frictionless packings are found to have an

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increasing nematic order as the aspect ratio is increased. For frictionless packings we find a non-monotonic dependence of the effective macroscopic friction as function of the aspect ratio but a monotonic increase in volume fraction at the rigidity transition while the reverse is found for frictional packings.

Wednesday 16:30 Kronborg

Fluidized bed rheology for granular media

<u>Schütz Denis</u>¹, Elke Riedl², Katja I. Hartmann³, and Andreas Kottlan⁴ ¹*Rheology, Anton Paar, Graz, Styria 8010, Austria;* ²*Anton Paar GmbH, Graz, Austria;* ³*Anton Paar Germany GmbH, Ostfildern, Germany;* ⁴*Rheology, Anton Paar, Graz, Styria 8010, Austria*

Dry granular beds are made "fluid-like" by an upstream of gas to produce gas fluidized beds. Widely used in a variety of industries they share certain similarities to suspensions, namely the combination of a viscous phase (gas) and a solid phase (particulates). A fluidized bed rheology setup consisting of a powder containing cylinder with a gas permeable bottom, through which a defined controlled gas flow is run into the powder sample, and a geometry placed in the powder. Attached to a rotational rheometer such a setup allows real rheological measurements over large ranges of shear rates and shear stresses on powder systems in a well-defined fluidization state. Being able to measure small torques in a reproducible manner enables a proper rheological study of fluidized beds similar to the rheology of complex fluids. To obtain absolute viscosity values a linear velocity profile is required and slip needs to be prevented. Different concentric cylinders smooth, rough and profiled surfaces were tested. Viscosity curves of a glass bead sample in the un-fluidized and the fully fluidized state measured with two profiled cylinders with different sizes are in good agreement indicating that the no slip condition is met. Results of viscosity curves in different fluidization states are presented and are compared to the behavior of liquid suspensions. While exhibiting some unique effects, the shear rate dependent behavior of a gas fluidized bed can be for the most part be linked to that of particulate suspension. Furthermore comparisons on multiple concentric cylinder geometries and a novel ball measurement system based upon stokesian surface viscosity relations that allows the measurement of more cohesive powders.

Wednesday 16:50 Kronborg

Dissipation potentials for viscoplastic media and granular flows

Joe D. Goddard

Mechanical and Aerospace Engineering, University of California, San Diego, La Jolla, CA 92093-0411, United States

The importance of dissipation potentials for treating viscoplastic flows was recognized in early works by Hill (1956) and Leonov (1988). These works, as well as the underlying mathematical foundation in much neglected works by Edelen in the 1970s, were pointed out in a recent article by Kamrin and Goddard (Proc. R. Soc. A 470: 20140434) which explores the symmetry of viscoplastic drag laws. Not only does the existence of dissipation potentials lead to extremum principles for quasi-static flows but it also facilitates the formulation of constitutive equations for viscoplastic flows with evolving anisotropy and higher gradient effects. This talk will present some examples, including the use of viscoplastic potentials in a higher-gradient model for regularization of the popular "mu(I)" model for granular flows, to modify the short wavelength (Hadamard) instabilities of a type that lead to shear banding. The same idea carries over to viscoplastic models for non-Newtonian fluids, such as wormlike micelles.

Wednesday 17:10 Kronborg

How tribo-electric charges modify powder flowability

<u>Geoffroy Lumay</u>¹, Filip Francqui², Julien Schockmel³, Antonella Rescaglio⁴, and Nicolas Vandewalle⁵ ¹Physics, University of Liège, Liege, Belgium; ²GranuTools, Awans, Belgium; ³University of Liege, Liege, Belgium;

⁴University of Liege, Liege, Belgium; ⁵CESAM - GRASP, University of Liege, Liege, Belgium

It is well known in industrial applications involving powders and granular materials that the presence of electrostatic charges influences drastically the material flowing properties. The apparition of electrostatic charges due to the triboelectric effect at the contacts between the grains and at the contacts between the grains and the container produces electrostatic forces. On the one hand, the triboelectric effect is useful for many applications (electrophotography, powder coating processes, triboelectric separators, ...), but on the other hand, the triboelectric effect is still poorly understood. The charging of objects composed by the same material and charging of powders are two examples of poorly understood subject. Even the basic question related to the nature of the transferred charges (electrons, ions or material) is still debated. The difficulties are related to the non-equilibrium character of the triboelectric dynamic and to the variety of mechanisms behind this effect. Moreover, reproducible electrostatic measurements are difficult to perform. We developed an experimental device dedicated to the measurement of powder triboelectric properties. This device measures the ability of a powder to charge electrostatically during a flow in contact with a selected material. This measurement is performed at controlled hygrometric conditions. We present the results of a systematic study involving a wide range of powders commonly used in industries. The link between grain properties, the hygrometry and the flowing behavior is analyzed. Finally, we discuss the link between these results and applications: pneumatic conveying, stability of pharmaceutical blends, ...

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Symposium MN

Micro and nanorheology, microfluidics

Organizers: Eric M. Furst and Anke Lindner

Wednesday 13:00 Schackenborg Directed assembly of pi-conjugated oligopeptides using microfluidics

Charles M. Schroeder¹, Bo Li¹, Lawrence R. Valverde², and William L. Wilson³

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A major challenge in the field of materials self-assembly is ability to control structural ordering at the nano- to mesoscale. Despite recent progress, there is a need for development of new continuous flow processes for directed assembly that extend beyond equilibrium-based batch methods. In this work, we study the self-assembly and fluidic-directed assembly of pi-conjugated synthetic oligopeptides using a combination of experiments and analytical modeling. The first part of the talk will focus on a systematic study of the non-equilibrium selfassembly of oligopeptides under reaction-dominated or diffusion-dominated conditions. Our results show that the morphology of assembled peptide fibers is controlled by the assembly kinetics, such that increasingly homogeneous structures are obtained using slower rates of assembly. We developed an analytical reaction-diffusion model to describe assembly, and experimental results are compared to the model across a range of Damkohler numbers. We further use passive microrheology to study materials properties during assembly, with direct comparison between microstructural and photophysical properties during the gel transition. The second part of the talk will focus on the development of a new continuous microfluidic process for the assembly and alignment of oligopeptides using 3-D flow focusing. To achieve continuous assembly, microfluidic devices are fabricated with integrated chevron patterns to generate a 3-D focused sheath flow of the reactant peptide. Following focusing, the peptide stream is directed toward an acidic triggering stream in a cross-slot geometry that mediates assembly into higher-order fiber-like structures using extensional flow, which ensures high degrees of microstructural alignment. In situ confocal microscopy and in situ fluorescence lifetime imaging microscopy (FLIM) are used to characterize peptides in real-time during assembly. Overall, this work shows that peptide assembly is governed by a delicate balance between kinetics and transport processes.

Wednesday 13:40 Schackenborg

A continuous roll-pulling approach for the fabrication of magnetic artificial cilia with microfluidic pumping capability

Ye Wang, Ruth Cardinaels, Jaap den Toonder, and Patrick Anderson

Department of Mechanical Engineering, TU Eindhoven, Eindhoven 5600MB, The Netherlands

In nature, microscopic hair-like cilia are abundantly present, providing essential functionalities to a wide range of organisms. Motile cilia cause fluid actuation, which allows for instance the swimming mobility of small organisms or sweeping the surfaces of larger organisms. Inspired by nature, a wide range of artificial cilia have been produced, using responsiveness to electric fields, light or magnetic fields for actuation. However, most production methods involve microfabrication techniques under cleanroom conditions, or use expensive sacrificial mould materials. In the present work, we present a continuous roll-pulling approach for the fabrication of magnetic artificial cilia (1,2). This cleanroom-free process does not require sacrificial materials and allows for high-speed large-area production of artificial cilia with a tailored geometry. A substrate covered with a thin liquid precursor consisting of a polydimethylsiloxane-based suspension is pulled underneath a rotating roll covered with micropillars. During this process, filaments are pulled from the precursor, resulting in slender cone-shaped cilia, which can then be cured to permanently fix their shape. The final cilia length depends on the length at breakup as well as the amount of retraction. In turn, these parameters are determined by the rheology of the precursor material, including flow properties as well as yield stress and timescale for buildup of the latter. A rheological study and fabrication tests were carried out for a range of precursor material compositions to obtain insight in the relations between precursor rheology and processing conditions on the one hand, and cilia geometry on the other hand. The generated artificial cilia were incorporated in a microfluidic device, where external magnetic actuation, leading to non-reciprocal cilia motion, allowed to generate substantial fluid flow. [1] Wang Y, den Toonder J, Cardinaels R, Anderson P, Lab on a Chip 16(12), 2277-2286 (2016) [2] https://www.youtube.com/watch?v=Irj7Y86aJLU

Wednesday 14:00 Schackenborg

Customised bifurcating networks for shear sensitive bio experiments

Joana Fidalgo¹, Konstantinos Zografos², Laura Casanellas³, Anke Lindner⁴, and Mónica Oliveira¹

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In this work, we assess the potential of customised microfluidic bifurcating networks as sensors for testing shear sensitive materials such as cells, vesicles, individual polymer molecules or even bulk solutions. The customised geometries were designed according to the biomimetic rule proposed by Zografos et al. [1], which allows the prediction of the wall shear stress along consecutive channel generations. This rule is valid for low inertia flows of both Newtonian and power-law behaviour in planar channels of rectangular cross section. We have tested two geometries, one with uniform and one with increasing wall shear stress, and good agreement was found between theoretical predictions, CFD simulations and experimental results in terms of flow kinematics for the two types of fluids. To evaluate the effect of the shear stress imposed in the two geometries, a dilute solution of shear sensitive ?-DNA was used as testing fluid. We confirmed that for the geometry

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is increased. Quantitative measurements of the ?-DNA deformation as a function of shear rate are in trend with previous results [2]. The results obtained are promising and the customised geometries may now be used to investigate the threshold limits of shear sensitive materials under well-known stress distributions. References: [1] K. Zografos, R. W. Barber, D. R. Emerson, and M. S. N. Oliveira, "A design rule for constant depth microfluidic networks for power-law fluids," Microfluid. Nanofluidics, vol. 19, no. 3, pp. 737-749, 2015. [2] D. E. Smith, H. P. Babcock, and S. Chu, "Single-

with uniform wall shear stress the molecules exhibit a similar deformation in the various network generations; while for the geometries with increasing wall shear stress, the degree of molecule deformation increases in the different generations of the network as the wall shear stress

Wednesday 15:50 Schackenborg

Scanning-SAXS of microfluidic flows: Nanostructural mapping of soft matter

Polymer Dynamics in Steady Shear Flow," Science, vol. 283, no. 5408, pp. 1724-1727, 1999.

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The determination of in situ structural information of soft matter under flow is challenging, as it depends on physico-chemical factors as well as on confinement, geometry, and flow type of the used flow geometry. We combine microfluidics and scanning small-angle X-ray scattering (scanning-SAXS) to create a two-dimensional spatially resolved map, which represents quantitatively the variation of molecular properties under flow. As application examples, mappings of confined amyloid fibrils and wormlike micelles under flow into various channel geometries are compared. A simple process to fabricate X-rays resistant chips based on polyimide and UV-curing resin is discussed. During experiments, these chips remained in high-energy synchrotron radiation for more than 24 hours causing constant low background scattering. Thus, sufficient statistics were obtained from sample scattering at exposure times as low as 0.1 s, even with the small scattering volumes in microfluidic channels. Scanning-SAXS of microfluidic flows has many potential applications from biology to fundamental soft matter physics. In general, any fluid which has enough contrast for X-ray scattering can be measured to obtain the dependence of molecular shape, conformation, alignment and size on the flow field. Besides, dynamic processes of soft matter caused by flow, temperature, concentration gradient, and confinement, for example self-assembling, aggregation, mixing, diffusion, and disintegration of macromolecules, can be quantified and visualized on a single image by this mapping technique.

Wednesday 16:10 Schackenborg

Flow-induced morphology of complex systems during phase inversion process

<u>Valentina Preziosi</u>¹, Antonio Perazzo², Giovanna Tomaiuolo³, and Stefano Guido⁴ ¹*DICMaPI*, Università degli Studi di Napoli Federico II, Napoli, Italy; ²*DICMAPI*, University of Napoli Federico II, Napoli, Italy; ³DICMaPI, Università degli Studi di Napoli Federico II, Napoli, Italy; ⁴DICMaPI, Università degli Studi di Napoli Federico II, Napoli, Italy

The possibility of creating complex structures at the nano- and micro-scale is an important feature of soft matter which can be exploited to provide peculiar properties for a range of applications. In particular, systems made of oil, water and surfactants display a complex phase behavior, which is not limited to the classical picture of emulsions made of droplets of one phase dispersed in the other one[1; 2]. Such complex system properties strongly depend on the microstructure of the dispersed and continuous phases and the investigation of microstructure evolution to obtain stable emulsions is of great relevance. Here we show that, starting from a system made of oil and surfactants (one hydrophilic and one hydrophobic), by increasing water concentration, surfactant self-assembly display different equilibrium phases showing lyotropic liquid crystalline properties, before an oil-in-water emulsion is found. This pathway is usually exploited in "phase inversion concentration" process[3; 4] as a means to obtain stable nano and microemulsions[5; 6]. To outline emulsion morphology development and the effect of flow on the microstructure, confocal microscopy and rheological measurements were exploited. Rheological measurements probed the increased viscoelasticity induced by water addition up to the point of bicontinuous phase formation. Confocal microscopy revealed the formation of complex mesoporous structures at the microscale. Moreover, the effect flow on the microstructure along the phase inversion emulsification process was investigated by performing experiments in a microfluidic set-up.

[1] A. Perazzo, V. Preziosi, S. Guido, Advances in Colloid and Interface Science. 2015, 222, 581. [2] P. Posocco, A. Perazzo, V. Preziosi, E. Laurini, S. Pricl, S. Guido, RSC Advances. 2016, 6. [3] A. Forgiarini, J. Esquena, C. González, C. Solans, Langmuir. 2001, 17. [4] S. Sajjadi, Langmuir. 2006, 22. [5] C. Solans, I. Solé, Current Opinion in Colloid & Interface Science. 2012, 17. [6] D. J. McClements, Soft Matter. 2012, 8.

Wednesday 16:30 Schackenborg

Microfluidic-based cell manipulation in viscoelastic fluids

Francesco Del Giudice, Shivani Sathish, and Amy Q. Shen

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Deformability is a critical parameter for discriminating healthy and diseased cells. Several complex microfluidics devices are currently available for separating cells with different deformability. Viscoelastic fluids have also been used for particle/cell separation to simplify the microfluidic design. In this work, we study the effect of cell deformability on the particle/cell transversal migration by flowing particle/cells with similar size but different deformability, suspended in two different viscoelastic fluids. Rigid particles with diameter d=20 ?m, NIH 3T3 fibroblasts with $d=19\pm2$?m and elastic modulus G ~52 kPa, BCL2 Jurkat lymphoblasts with $d=15\pm2$?m and G ~0.29 kPa are used. The first suspending fluid is an aqueous solution with 0.08 wt% hyaluronic acid (HA) with the addiction of phosphate buffer saline (0.138 M NaCl, 0.0027 M KCl); this liquid has a constant-viscosity in the range of shear rate investigated. The second is an aqueous solution with 0.8 wt% HA (shear-thinning liquid). Particles and cells are observed at 8 cm from the inlet of a straight 150 ?m square-shaped microchannel. Both cells and rigid particles suspended in the constant-viscosity liquid migrate mostly towards the centerline due to the

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synergic effects of elastic forces and deformability-induced forces. In the shear-thinning liquid, most of the particles migrate towards the walls. In contrast, cells suspended in the shear-thinning liquid at 8 cm from the inlet are found between the walls and the centerline, due to the competition between the elastic force (directed towards the wall in shear-thinning liquids) and deformability induced force (directed towards the centerline). The Jurkat cells (softer) are found to migrate closer to the centerline than NIH 3T3 cells (more rigid).

Wednesday 16:50 Schackenborg

Flow of wormlike micellar solutions around confined microfluidic cylinders

<u>Amy Q. Shen¹</u>, Simon J. Haward², and Ya Zhao³

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Wormlike micellar (WLM) solutions are frequently used as fracture and proppant-carrying fluids in enhanced oil and gas recovery applications in porous rock beds where complex microscopic geometries result in mixed flow kinematics with strong shear and extensional components. To gain understanding of WLM fluids flowing through porous media, we examine the flow around a single micro-scale cylinder aligned on the flow axis1. We study flow behavior of an aqueous WLM solution consisting of cationic surfactant cetyltrimethylammonium bromide (CTAB) and a stable hydrotrope 3-hydroxy naphthalene-2-carboxylate (SHNC) in microfluidic devices with three different cylinder blockage ratios, β . The WLM solution is strongly viscoelastic and exhibit shear banding behaviour. Flow of WLM solutions around confined cylinders results in the onset of a sequence of low Re flow instabilities, which depend on both Wi (as high as 105) and β . Interestingly the flow instabilities first emerged upstream of the cylinder, which are associated with high stresses in fluid that accelerates into the narrow gap between the cylinder and the channel wall, while upstream vortex growth is reminiscent of that seen in microfluidic contraction geometries. Instabilities downstream of the cylinder are associated with stresses generated at the trailing stagnation point and the resulting flow modification in the wake, coupled with the onset of time-dependent flow upstream and the asymmetric division of flow around the cylinder. The strong shear thinning and shear banding nature of the WLM solution also contributes to the observed instabilities.

[1] Ya Zhao, Amy Q. Shen, Simon J. Haward, Soft Matter, 2016, 12, 8666-8681.

Wednesday 17:10 Schackenborg

Elastic Instabilities in Pillared Micro channels in Effect to Polymer Flooding

Shauvik De¹, John van der Schaaf¹, Hans Kuipers¹, Frank Peters¹, and <u>Johan T. Padding²</u> ¹Chemical Engineering and Chemistry, Eindhoven University of Technology, EINDHOVEN, The Netherlands; ²TU Delft, Delft, The Netherlands

Polymer liquids are used in the oil industry to improve the volumetric sweep efficiency and displacement efficiency of the oil from a reservoir. Surprisingly, it is not only the viscosity but also the elastic properties of the displacing fluid that determine the displacement efficiency. To understand the effects of viscoelasticity on enhanced oil recovery, both single and multiphase experiments are performed in pillared microchannels of different pitches. Different shear thinning viscoelastic fluids are used to obtain insights into flow structures in these pillared micro channels. Particle image velocimetry (PIV) technique is applied to characterise the complex flow structures at very low Reynolds number (< 0.01). The pressure drop across the channel for a range of Deborah numbers is measured using a pressure sensor. We observe an onset of flow asymmetry for the viscoelastic fluid after a critical Deborah number depending on the channel configuration. This flow asymmetry increases with an increase in Deborah number and shows characteristics of elastic turbulence. This can be characterised by an increase in velocity and pressure fluctuations which has a temporal and spatial dependency. The sudden increase in the velocity fluctuations is also visible from the micro-PIV experiments. Though the fluid is shear thinning in nature, we observe an increase in the apparent viscosity after the critical De number is reached, which represents a thickening behaviour. So strong shear and extensional effects of the viscoelastic fluid are responsible for the asymmetric flow structures. Next we performed multiphase flow experiments, by saturating the microchannel with oil, and then displacing it by different non-Newtonian fluids. Surprisingly we found the enhanced recovery corresponds to the critical De number where the onset of instability initiates for the single phase experiments. The elastic instabilities and the relation to enhanced displacement provides fundamental insights in the mechanism of polymer flooding.

Wednesday 17:30 Schackenborg

MN15

Velocity profiles and shear-induced structuring in wormlike micellar solutions flowing in a microcapillary <u>Carla Caiazza¹</u>, Valentina Preziosi¹, Giovanna Tomaiuolo¹, Denis O'Sullivan², Vincenzo Guida², and Stefano Guido¹ ¹DICMaPI, Università degli Studi di Napoli Federico II, Napoli, Italy; ²Brussels Innovation Center, Procter & Gamble, Brussels, Belgium

In the last decades, both in basic and applied research a growing attention has been devoted to wormlike micellar solutions, thanks to their widespread utilization in cleaning and personal care products. In spite of all these efforts, the unique rheological and flow properties, characterized by the occurrence of flow instabilities [1] at high shear rates (such as shear banding [2]) have not been fully elucidated.

In this scenario, microfluidics is a powerful tool to get a deeper insight into the flow behaviour of a wormlike micellar solution, as it provides the opportunity to both enhance confinement effects [3] (and, thus, surface forces driven instabilities) and directly visualize the system under flowing conditions. In fact, the small dimensions of a microfluidic device allow one to couple confined flow and optical microscopy, and to perform flow visualization and structural imaging at the micro-scale.

Here, by feeding a widely used wormlike surfactant solution in a microcapillary geometry we measure the velocity profiles by particle tracking techniques. The results are related to a complex flow structuring and to the rheological properties of the system investigated.

MN14

- E. K. Wheeler et al., J. Non-Newtonian Fluid Mech. 75 (1998)
 T. Dioux et al., Annu. Rev. Fluid Mech. 48 (2016)
 Y. Zhao et al., Adv. Colloid Interface Sci. 211 (2014)

Thursday Morning

Symposium PL

Plenary Lectures

Thursday 9:00 Grand Ball Complex

Viscoelasticity of transient networks from associating polymers: a mesoscopic modeling perspective Evelyne Van Ruymbeke

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Understanding and tailoring the viscoelastic response of polymer melts or concentrated solutions from the knowledge of their molecular structure (architecture) represents a formidable challenge and remains a prime field of soft matter research, with several important and fundamental questions still open. To this end, we have developed a general coarse-grained approach based on the tube model, that we are now using as a predictive tool in order to investigate the viscoelastic properties of complex, entangled polymer architectures. Our main objective is to elucidate the molecular origin of their relaxation processes and in particular, their constraint release mechanisms.

In this presentation, we first outline the construction of the time marching algorithm which represents the key ingredient of our approach, and then discuss some selected examples. Next, we extend this approach to describe the complex rheology of entangled macromolecular self-assemblies built from sticky polymers, and use our model as a new tool for an in depth analysis of their viscoelastic properties. In particular, we investigate the dynamics of a series of model telechelic linear and star polymers which create a reversible network through metal-ligand association, and study the effect of blending different architectures on the network relaxation. We also investigate the behavior of entangled polymers bearing stickers along their backbone. In all cases, we show that the dynamics of these associating polymers strongly depends on the ratio between entanglements and stickers density, as well as on the ratio between their association and disentanglement times, leading to a large variety of viscoelastic reponses.

Symposium SC

Suspensions and colloids

Organizers: Norbert Willenbacher and Philippe Coussot

Thursday 10:30 Grand Ball

Structural and dynamic properties of dense suspensions of ellipsoidal particles

Thiago Ito, Antara Pal, Alfredo Lanzaro, Jérôme J. Crassous, and Peter Schurtenberger *Physical Chemistry, Department of Chemistry, Lund University, Lund SE-22100, Sweden*

Dispersions of prolate particles with relatively low axial ratios are interesting colloidal model systems as they have been predicted to show a quite rich phase diagram with isotropic, nematic and an additional simple monoclinic crystal phases depending on the packing fraction [1]. Despite the increased interest in the properties of anisotropic colloids, there is still a lack of systematic experimental data primarily due to the lack of suitable model systems. Here we present the results from a systematic study of the packing fraction dependence of the structural and dynamic properties using a combination of methods such as small-angle X-ray scattering, 3D cross-correlation dynamic light scattering and rheometry employing both microfluidics as well as traditional rheology methods. The microfluidics device allows us to perform simultaneous flow visualization and rheometry experiments, which we use to explore and characterize the flow phenomena that occurs at large packing fractions and Peclet numbers. We use hematite-based magnetic particles coated with a silica shell as a model system [2], where we remove the core to reduce the density mismatch. The resulting particles are prolate ellipsoids with overall dimensions of L \sim 280 nm for the long axis, d \sim 70 nm for the short axis, and a thin silica shell with thickness t \sim 30 nm, which can be dispersed in solvents such as DMSO to provide a strongly reduced contrast for light scattering and thus allow measurements at very high packing fractions. We describe the full state diagram for these particles as a function of packing fraction as well as the evolution of the static and dynamic structure factor and the low and high shear viscoelastic properties as the system approaches the glass transition.

1. G. Bautista-Carbajal, A. Moncho-Jordá and G. Odriozola, J. Chem. Phys., 138, 064501 (2013). 2. I. Martchenko, J. J. Crassous, A. M. Mihut, E.Wernersson, A. Hirt, C. Rufier, A. Menzel, H. Dietsch, P. Linse and P. Schurtenberger, Soft Matter, 12, 8755 (2016)

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SC33

Thursday 10:50 Grand Ball

Stiffness and Geometry Influences on the Shear Flow Behavior of Colloidal Rods

Christian Lang¹, Joachim Kohlbrecher², Lionel Porcar³, and Minne P. Lettinga⁴

¹ICS-3 Soft Matter, Forschungszentrum Jülich, Jülich, NRW 52428, Germany; ²Laboratory of Neutron Scattering and Imaging, Paul Scherrer Institut, Villigen, Switzerland; ³Large Scale Structures, Istitut Laue Langevin, Grenoble, France; ⁴ICS-3 Soft Matter, Forschungszentrum Jülich, Jülich, Germany

The flow of rodlike particle suspensions is of broad practical interest as they are highly susceptible to shear flow. Geometry and stiffness of rods, thereby, play a key role in the microscopic behavior which leads to the macroscopic rheological response. We present a combination of Rheology and Small Angle Neutron Scattering (Rheo-SANS) to resolve the orientational ordering of rodlike viruses under steady shear flow in the 2 relevant planes, the flow-gradient and the flow-vorticity plane. The full orientational order tensor can be resolved in this way, as has been shown earlier [C. Lang, J. Kohlbrecher, L. Porcar, M. P. Lettinga; Polymers 8 (2016); 291]. By bio-engineering viruses with different geometries and stiffnesses, we are able to study the influence of those parameters on the shear thinning behavior of dilute to semi-dilute rodlike colloidal suspensions without polydispersity issues.

Thursday 11:10 Grand Ball

SC35

Viscometric functions of monodisperse and bidisperse non-colloidal suspensions

Chaiwut Gamonpilas¹, Jeffrey F. Morris², and Morton M. Denn²

¹National Metal and Materials Technology Center, Klong Luang, Pathumthani 12120, Thailand; ²Levich Institute, CUNY City College of New York, New York, NY 10031, United States

Normal stress differences (N_1 and N_2) are familiar quantities, but are rather poorly studied for sheared suspensions. In particular, the normal stress response has received limited attention for bidisperse suspensions. In this work, we present the results of measuring the viscometric functions of mono- and bimodal non-colloidal suspensions of polymethyl methacrylate (PMMA) spheres in a density-matched aqueous Newtonian suspending fluid. The measurements were performed using combined parallel-plate and cone-and-plate rheometry for particle concentrations in the range 0.20 to 0.50. Cone-and-plate normal stress measurements employed the method of Marsh and Pearson, in which there is a finite gap between the cone tip and the plate. The monodisperse suspensions showed an unexpected particle size dependence of the viscometric functions, with the viscosity increasing with decreasing particle size. Such strong particle size dependence for the PMMA spheres in the aqueous Newtonian surfactant suspending fluid is unexpected in light of prior studies and points to an effect of fluid-particle surface chemistry. Furthermore, the normal stresses were very small in magnitude and difficult to measure at volume fractions below 0.30. At higher concentrations, N_2 was negative and much larger in magnitude than N_1 . Interestingly, the algebraic sign of N_1 was positive over most of the shear rate range for the monodisperse suspensions but indeterminate and possibly negative for the bimodal suspensions. The normal stresses were insensitive to bidispersity when plotted as functions of the shear stress at each volume fraction. The effectiveness of using Marsh and Pearson method will also be discussed by comparing the results with a direct measurement of N_1 from a classical cone-and-plate geometry.

Thursday 11:30 Grand Ball

X-ray Imaging of flowing suspensions

Guillaume Ovarlez¹, Stéphanie Deboeuf², Nicolas Lenoir³, Mohammad Gholami⁴, and Sarah Hormozi⁵

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A key element to understand the rheological behavior of suspensions is their microstructure: the spatial distribution of particles depends on flow history, which has an impact on the suspension macroscopic properties. This appeals for the development of experimental tools allowing for the 3D imaging of particles in viscosimetric flows.

At a macroscopic scale, concentrated suspensions often display concentration inhomogeneities, due to shear-induced migration. These inhomogeneities can lead to the formation of jammed regions, which have a strong impact on the measured behavior. It is crucial to describe this phenomenon near the jamming transition and in shear-thickening fluids. It is thus necessary to develop new tools to get time-and spatially-resolved concentration fields in flowing suspensions.

In this talk, we present recent developments to tackle these issues with the help of X-ray imaging.

We first present the technique we developed to image in 3D the microstructure of suspensions of non-Brownian particles, using X-ray computed tomography and sub-voxel identification of particle centers. We illustrate its interest on a few examples. We show that one can get an isotropic microstructure after mixing. Under shear, the microstructure becomes anisotropic in the shear plane, whereas it is isotropic in the 2 other planes. While for Newtonian suspensions the anisotropy is independent on the shear rate, we show that for a yield-stress suspension it depends on it. Finally, we evidence particle alignment along both solid surfaces and free interfaces.

We then present the technique we developed to get time-resolved 2D concentration fields in a rheometric flow, thanks to 2D X-ray radiography. We illustrate its interest for shear-thickening fluids. We show that most suspensions display strong inhomogeneities at the onset of Discontinuous Shear thickening (DST), which poses the question of the intrinsic (local) behavior of DST suspensions and might lead to revisit the interpretation of this behavior.

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SC34

Thursday 11:50 Grand Ball

Anomalous structural response of nematic platelets under Large Amplitude Stress and Strain Oscillations revealed by 3D RheoSAXS

<u>Olivera Korculanin</u>¹, Daniel Hermida-Merino², Helmut Hirsemann³, Bernd Struth³, Simon A. Rogers⁴, and Minne P. Lettinga⁵ ¹ICS-3, Forschungszentrum Jülich, Jülich 52428, Germany; ²Dubble, ESRF, Grenoble, France; ³Photon-Science Detector-Group, DESY, Hamburg, Germany; ⁴Department of Chemical and Biomolecular Engineering, University of Illinois Urbana-Champaign, Urbana, IL, United States; ⁵ICS-3 Soft Matter, Forschungszentrum Jülich, Jülich, Germany

Dispersions of colloidal Gibbsite platelets in the nematic phase display a complex response to Large Amplitude Oscillatory Shear (LAOS) flow that strongly depends on the strain amplitude. [1] In this work we applied time-resolved small angle x-ray measurements to investigate the dynamic response to nonlinear oscillatory stresses and strains of a nematic dispersion of colloidal Gibbsite platelets. We track the full 3D rotational motion of the director by employing plate-plate and concentric cylinder Couette geometries as well as a vertical X-ray beam. [2]

Under nonlinear oscillatory stress we observe strong offsets in the rheological response as well as asymmetrical behavior in the microscopic structural response. This offset and asymmetry are connected to the yielding behavior of the platelets. By increasing the stress amplitude we observed that the offset of the rheological response diminishes and the microscopic response becomes more symmetric; however, this strongly depends on the frequency of the stress input, and hence the time necessary for the system to yield.

Softening of the response towards the centre of the gap was observed by scanning the gap while performing LAOStrain. The structural response at low strain amplitude does not propagate throughout the gap, where as at high strain amplitudes the response in the bulk emerges as erratic.

References:

[1] M. P. Lettinga, P. Holmqvist, P. Ballesta, S. Rogers, D. Kleshchenok, and B. Struth. Non-linear behavior of colloidal plateles in shear flow. Phys. Rev. Lett. (2012) Vol. 109, 246001.

[2] Struth, B. et al., Observation of New States of Liquid Crystal 8CB under Nonlinear Shear Conditions as Observed via a Novel and Unique Rheology/Small-Angle X-ray Scattering Combination. Langmuir, 2011, 27 (6), pp 2880-2887 DOI: 10.1021/la103786w

Thursday 12:10 Grand Ball

SC38

Electrorheological behaviour of suspensions of doped polyaniline nanofibers containing carbon nanoparticles dispersed in silicone oil

Jenifer Santos-Garcia¹, Sumita Goswami², Nuria Calero³, and Maria Teresa Cidade⁴

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Using external electric or magnetic fields to control the viscosity of fluids or suspensions has been attracting much attention in scientific and technological fields because of its potential use in active control of various devices. These fluids, whose viscosity can reversibly respond to external electric or magnetic fields, are often referred as 'smart fluids' which include magnetorheological (MR) fluid and electrorheological (ER) fluids. ER fluid consisting of polarizable particles dispersed in a non-conducting liquid can be transformed reversibly and rapidly from a fluid-like state to a solid-like state due to the disorder-order transition of particulate phase under an applied external electric field, showing tunable changes in the rheological characteristics. The tunable and quick rheological response to external electric fields makes ER fluid possess potential uses to enhance the electric-mechanical conversion efficiency in mechanical devices such as clutches, valves, human muscle stimulator, etc. This work presents the influence of carbon nanoparticles concentration on the ER behaviour of suspensions of PANI (polyaniline) doped with CSA (camphorsulfonic acid) nanofibers in silicone oil. In addition, the effect of the dopant (CSA and citric acid) has also been studied for these dispersions. The ER properties of the suspensions were carried out using a rotational rheometer, to which an ER cell was coupled, in steady and oscillatory shear, and electrical field up to 2 kV/mm. All the samples showed an ER effect, which increased with electric field and nanofibers concentration and doped with citric acid. PANI/CSA composite nanostructures dispersed in silicone oil exhibited the highest ER activity, higher than 3 decades increase in viscosity for low shear rates and high electric fields, showing their potential application as ER smart materials.

Symposium NF

Non-Newtonian fluid mechanics and fluid instabilities

Organizers: Natalie Germann and Suzanne Fielding

Thursday 10:30 Amalienborg

Numerical study of multiphase flows of viscoelastic fluids using an improved Level-Set method Artur Sucena¹, Alexandre Afonso¹, Manuel A. Alves², and Fernando T. Pinho¹

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Numerical simulations are presented in this work, aiming to study the behaviour of multiphase flows of rheologically complex fluids, considering the liquid-droplet flow of viscoelastic fluids. By changing the properties of both the liquid droplet and the continuous fluid (the ratio of the viscosities and relaxation times), different flow configurations were simulated.

The Level-Set method [1] used to compute the liquid-liquid flows was implemented in our in-house viscoelastic flow solver. In the Level-Set method, the interface is represented by a closed curve using the so-called level-set function, which is defined as the signed distance to the interface. This function is governed by a Hamilton-Jacobi partial differential equation particularly suitable for the simulation of changing topologies, which is solved numerically. In particular, in this work a new redistancing method is introduced to preserve the definition of the level-set function throughout the iteration process, thus improving both the precision and computational times.

The code is initially verified by solving the droplet transport problem for a Newtonian fluid. Subsequently, we employ the Upper-Convected Maxwell, Oldroyd-B and the Phan-Thien-Tanner models to describe the rheology of different fluids, and assess the corresponding behaviours of the droplet transport in a constriction micro-geometry. Finally, a detailed study of the viscoelastic instabilities on the relevant rheological parameters of the non-linear viscoelastic models is reported, regarding the effect of both the relaxation time and fluid polymer viscosities ratio of both the droplet and the continuous fluid.

References

[1] S. Osher and J.A. Sethian, "Fronts propagating with curvature dependent speed: algorithms based on Hamilton-Jacobi formulations", J. Comput. Phys. 79, 12-49, 1988.

Thursday 10:50 Amalienborg

Simulation of the motion of a spheroid in a viscoelastic liquid in a pressure-driven channel flow

<u>Gaetano D'Avino¹</u>, Francesco Greco², Martien A. Hulsen³, and Pier Luca Maffettone¹ ¹Dipartimento di Ingegneria Chimica, dei Materiali e della Pr, Universitá di Napoli Federico II, Naples, Italy; ²Istituto di

Ricerche sulla Combustione, IRC-CNR, Naples, Italy; ³Department of Mechanical Engineering, Technische Universiteit of Eindhoven, Eindhoven, The Netherlands

The motion of anisotropic particles suspended in fluids is relevant in several fields. The most of the available works have analyzed the dynamics of elongated particles suspended in Newtonian fluids. Nevertheless, many applications involve suspending media showing a viscoelastic rheological behavior. To date, theoretical, numerical and experimental studies on this topic have been mainly performed in a simple shear flow field, showing a quite complex dynamics as compared to that observed with spherical particles. Despite the obvious relevance, studies on the dynamics of non-spherical viscoelastic suspensions in channel flows is extremely limited. In this work, we present 3D direct numerical simulations on the motion of a spheroidal particle suspended in a viscoelastic liquid in a pressure-driven flow between two infinite parallel plates. The finite element method is used to solve the governing equations with an automatic remeshing algorithm to account for the severe mesh distortion induced by the particle orientation change. The effect of the initial particle position and orientation, and the Deborah number on the translational and rotational dynamics of the spheroid is investigated. The migration phenomenon induced by the interplay between anisotropic shape, confinement and viscoelasticity is discussed.

Thursday 11:10 Amalienborg

Simulation of adhesive using a novel viscoelastic stress method

Simon Ingelsten¹, Andreas Mark¹, Per-Johan Wahlborg², and Fredrik Edelvik¹ ¹Computational Engineering and Design, Fraunhofer-Chalmers Centre, Gothenburg, Sweden; ²Swerea IVF, Mölndal, Sweden

In the industry the demands on environmentally friendly products and processes increase which in turn increases the focus on lightweight composite materials. Such materials often cannot be welded, and the use of adhesives is therefore an alternative. This requires new production processes for which a thorough understanding is needed in order to optimize the effectivity and ensure sufficient strength and quality of the joints. A key part in understanding the processes is the ability to simulate the flow of adhesive materials, which have complex rheology and may be both viscoelastic and thixotropic. It is thus not sufficient to describe its rheology with a purely shear thinning model. This is due to that such models does not account for storage of energy and transient stress relaxation. In this work the flow solver IPS IBOFlow is used for simulating the extrusion of adhesive. In IBOFlow internal objects are treated using implicit immersed boundary conditions. The flow equations are solved on a Cartesian octree grid which is automatically generated and adapted. The two-phase flow of adhesive and air is modelled with the Volume of Fluid method. The adhesive is modelled by a novel approach in which the constitutive equation for the viscoelastic stresses is solved on a Lagrangian grid represented by massless particles being convected by the fluid. The full stress tensor is interpolated to the fluid grid and explicitly added to the momentum equations. The method is computationally effective for multiphase flows compared to solving the constitutive equation on the Eulerian grid. The non-linear viscoelastic PPT model, which has

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been widely used in the literature to simulate viscoelastic polymeric fluids, is used as constitutive equation for the stresses. The method is validated with experimental data of the viscoelastic flow past a confined cylinder and by comparison between simulated adhesive beads and scanned experimental beads in the cross section. In both cases the simulations agree very well with the experiments.

Thursday 11:30 Amalienborg Fluidity model for non-Newtonian glass forming liquids Heliana Cardenas and Thomas Voigtmann

Institut für Materialphysik im Weltraum, Deutsches Zentrum für Luft- und Raumfahrt, Köln 51147, Germany

Glass forming liquids have a time scale many orders of magnitude slower than that of single particle motion: their dynamics depends on slow collective structural relaxation processes causing viscoelasticity. Consequently their rheology is highly non-linear and, under strong driving, the flow becomes non-Newtonian characterized by yield stress, and shear thinning. Microscopic yielding can produce heterogeneous flow patterns like shear bands and cooperativity in the flow: active areas will induce stress to their neighbors up to a length scale "cooperativity length"; hence the stress must be non-local and diffuse at a rate defined by plastic activity. A phenomenological fluidity model is used to capture the competition between the quiescent structural relaxation and flow induced relaxation. This model reproduces typical non-Newtonian features like plug flow in the center of a pressure-driven flow: yield stress. In simple start-up shear we observe transient shear bands that disappear when steady state is reached, whereas wall effects can induce long lived bands. Memory effects like residual stresses are also reproduced, e.g. if we remove the applied shear rate after reaching a non-equilibrium stationary state in a simple start-up shear, the fluid velocity drops to zero yet the shear stress remains present. We have studied the sedimentation of non-Brownian particles in the glass-forming fluidity model using a Fictitious Domain Method (FDM) coupled to a Lagrangian Discrete Element Method (DEM). Particles sedimenting will fluidize their neighboring areas up to a cooperativity length around them. Drafting-kissing-chaining effect is expected and reproduced when 2 particles separated by an initial vertical distance start sedimenting on top of each other. In shear thinning fluids this effect is more pronounced than in viscoelastic fluids because a lower viscosity passage is formed behind the trailing particle accelerating the following one. We use CFD-DEM-coupling and OpenFOAM to perform all mentioned calculations.

Thursday 11:50 Amalienborg

Numerical simulations of buoyancy-driven droplets in non-Newtonian media using a variance-reduced, micro-macro, particle-level set method

Juan Luis Prieto

Universidad Politécnica de Madrid, Madrid, Spain

In this presentation we introduce the main features and explore the capabilities of a recently developed multi-scale, particle level-set method termed SLEIPPNNIR [Comput. Methods. Appl. Mech. Eng, 307 (2016),164-192] for the simulation of non-Newtonian fluids. The method uses a second-order accurate, Finite-Element discretization in space, along with a semi-Lagrangian approach ("method of the characteristic curves") to deal with the convective terms. Surface tension effects are considered through the Laplace-Beltrami operator to circumvent the need for curvature computations. Non-Newtonian fluids are modeled by means of a variance-reduced, micro-macro approach, in which a collection of ensembles of polymer particles, whose internal degrees of freedom are obtained by a suitable kinetic model (e.g. Hooke, FENE), are scattered over the domain. The resulting polymer (extra-stress) tensor is then computed via a Compactly-Supported Radial Basis Function (CSRBF) approach providing a high-degree of mesh independency. Finally, we show numerical simulations of buoyancy-driven droplets rising in both Newtonian and non-Newtonian media, for a range of inertial, surface tension and viscoelastic effects.

Thursday 12:10 Amalienborg

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Rise and coalescence of bubbles in a low Reynolds number flow: observations and simulation

Romain Castellani¹, Mehdi Khalloufi¹, Antoine Marchal², Arnaud Poulesquen², and Rudy Valette¹

¹CEMEF, PSL Research University, MINES Paristech, Sophia Antipolis, France; ²DEN, DTCD, SPDE, LP2C, CEA, Bagnols-sur-Cèze, France

To describe the behaviour of gas bubbles, one must take into account distinct phenomena: nucleation, growth, rise and coalescence. Their kinetics dictates foamy materials behaviours, such as flour dough or bitumen used to immobilize nuclear waste. Modelling the processes is essential to control or predict porosity and material volumes as they are key-parameters in, respectively, the making of man-made products or to prevent disasters. Simulations on radiation induced gas creation in bitumen have shown the way populations of bubbles evolve [1]. However, as many phenomena occur there, an observation of their behaviour, especially coalescence and rise, could be of the greatest interest. Many articles have addressed this topic for systems at high Reynolds number and capillary forces (e.g. gas bubbles in water or liquid/liquid systems). However, for bitumen, viscosity can reach important values depending on the temperature (10⁶ Pa.s at room temperature with an activation energy of 155 kJ/mol).

In a first approach, we observed bubbles rise and coalescence in a PDMS Newtonian matrix (~300 Pa.s). Reynolds number obtained is as low as 10^{-6} and capillary forces are negligible (Ca=150). A simple device constituted of a glass tank and a camera was used for the measurements. Nitrogen is injected through pierced pipes or needles depending on what is observed: isolated bubbles or series of bubbles. After analysis, rising speeds can be well predicted and fall in-between Stokes and Hadamard-Rybczynski models. Complex interactions between bubbles are also observed, as the interfaces are considerably deformable. To better understand the flows and interactions between bubbles, such as interfacial draining, direct simulations were performed using a finite element method.

[1] A. Marchal et al., Competitive growth and rising of bubbles in a yield stress fluid. Consequences on the macroscopic swelling of bitumen drums, *Journal of Non-Newtonian Fluid Mechanics* Vol. 234: 162-169 (2016)

NF37

Symposium GS

Gels and self-assembled systems

Organizers: Moshe Gottlieb and Henning H. Winter

Thursday 10:30 Christiansborg

Mechanical properties of aerogels and xerogels derived from amino-acid organogels and from syndiotactic polystyrene gels

<u>Philippe Martinoty</u>¹, Dominique Collin¹, Danielle Barth², and Antoni Sanchez-Ferrer³ ¹Institut Charles Sadron CNRS, Strasbourg 67034, France; ²Laboratoire Réactions et Génie des Procédés, CNRS, UMR 7274, Nancy 54001, France; ³Swiss Federal Institute of Technology, Zürich CH-8092, Switzerland

The mechanical properties of aerogels and xerogels obtained upon drying amino acid organogels and syndiotactic polystyrene (sPS) gels have been studied with a piezoelectric rheometer as a function of frequency, concentration of the organogelator molecules and of the polystyrene chains. The aerogels and the xerogels were obtained by the CO2-supercritical drying process and by simple evaporation of the solvent, respectively. Simultaneous measurements of the volume V and the complex shear modulus G* of the aerogels, xerogels and of the genitor systems (organogel and gel) were performed for the first time in order to follow the behavior of the product V.G' upon drying. The CO2 supercritical drying process leads to aerogels defined by the relationship (V·G')aerogel = (V·G')genitor system, or in condensed form as V·G' = constant. This constant can be equal to 1 (the classical picture), as for the 10% sPS gel in toluene or in tetralin, or higher than 1, as for the organogel in toluene or tetralin. This difference comes from the fact that organogels are dynamically arrested suspensions, whereas gels rest on the notion of fractal growing. When the concentration of the sPS gels becomes smaller than 10%, the relationship G'V = constant is no longer verified, showing that these systems are not aerogels, but partially collapsed solids defining a class of mesoporous solids intermediate between aerogels and the fully collapsed solids (xerogels) obtained by slow evaporation of the solvent. This study shows that the product VG' is the key parameter for classifying the dried systems.

Thursday 10:50 Christiansborg

Time-resolved rheological monitoring of viscoelastic materials under drying

Bosi Mao¹, Annie Bouchaudy², Jean-Baptiste Salmon², Thibaut Divoux¹, and Patrick Snabre¹

¹Centre de Recherche Paul Pascal, CNRS, Pessac, Gironde 33600, France; ²Laboratoire du Futur, CNRS, Pessac, Gironde 33600, France

Monitoring the drying of soft materials from colloidal suspensions to polymer gels in a non-invasive way is a real experimental challenge. Here we introduce a novel setup that allows us to monitor the shrinkage and the viscoelastic properties of a drying soft material. The sample is sandwiched between two parallel-plates of much larger diameter than the sample thickness, which allows for the homogeneous drying of the sample along the radial direction. Moreover, the upper plate is connected to a commercial stress-controlled rheometer that maintains a constant zero normal-load on the sample, which contracts due to the slow and progressive loss of water. The decrease of the gap width imposed by the rheometer so as to maintain a zero normal load on the sample provides a direct measurement of the sample contraction, while shear oscillations of small amplitude gives time-resolved measurements of the sample viscoelastic properties during the whole drying process. We validate the test-fixture following the drying of distilled water and water/glycerol mixtures, and we further use the test-fixture to monitor the drying of two viscoelastic materials. First, we show that the drying of a colloidal suspension involves a transient gel state, which formation can be easily monitored using our setup. Second, time-resolved measurements of the elasticity of agar gels left to dry at constant temperature reveal that a 10% wt. water-loss leads to a 50% drop of the sample elasticity associated with strong microstructural changes. The present test-fixture associated with the zero normal load protocol open new perspectives for monitoring the drying of viscoelastic soft materials.

Thursday 11:10 Christiansborg

GS20

GS19

GS18

Negative normal stress difference in a low concentration suspension: Using capillary suspension to achieve a gel-like state

Irene Natalia¹, Nicole Zeiler², and Erin Koos³

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Typically, negative normal stress differences are reported at high shear rates for highly concentrated dispersions [1,2]. Such normal stress differences are reported here at a solid concentration of 25% - a volume fraction that is generally considered too low to show such normal stress differences - in a system with strong capillary attraction. In such capillary suspensions, a small amount of immiscible secondary fluid added to the continuous phase of a suspension changes the rheological behavior from a fluid-like to gel-like state [3]. This transition is caused by attractive capillary force between the particles and the two fluids inducing a sample-spanning network. Capillary suspensions exist in two states: a pendular state when the secondary fluid preferentially wets the particles, and a capillary state when the bulk fluid is preferentially wetting.

Capillary suspensions have the ability to rebuild their networks upon cessation of high shear rates. To systematically study this phenomenon, the normal stress difference is investigated during a flow sweep experiment with decreasing shear rates. In the pendular state, the system undergoes a transition from a positive normal stress difference at the high shear rates to a negative one at the low shear rates. In

highly concentrated systems, such negative normal stress difference indicates the formation of flocs along the vorticity direction. Analogue experiments also have been run for the capillary state. The system showed only negative normal stress difference. These results, therefore, might be indicative of more rigid flocs in the pendular state that are able to undergo solid-body rotation to reorientate under shear and either a lack of orientation or a weaker, less rigid, network in the capillary state.

[1] Montesi, A., et al. Physical Review Letter 2004, 92, 58303

[2] Osuji, C., Weitz, D.A. Soft Matter 2008, 4, 1388

[3] Koos, E., Willenbacher, N. Science 2011, 331, 897-900

Thursday 11:30 Christiansborg

<u>Stefano Aime</u>¹, Laurence Ramos², and Luca Cipelletti³ ¹Laboratoire Charles Coulomb, Montpellier 34090, France; ²UMR 5221, CNRS, Laboratoire Charles Couloumb, Montpellier, Languedoc-Roussillon 34000, France; ³Laboratoire Charles Coulomb, Montpellier 34090, France

Microscopic dynamics and failure precursors during the creep of a colloidal gel

We study the microscopic dynamics of a model colloidal gel under a shear stress, using small-angle dynamic light scattering coupled to a custom-made, stress-controlled shear cell. We find that the gel creep consists of three regimes. After an instantaneous elastic jump, in the primary creep regime the deformation increases as a power law of time, and is well described by linear viscoelasticity. This regime lasts several hours; microscopically, the deformation deviates from affine behavior, but these non-affine dynamics are fully reversible. In the second regime, deviations are observed with respect to linear viscoelasticity, concomitant with a sharp acceleration of the non-affine dynamics, which become irreversible. These faster rearrangements precede the macroscopic rupture of the gel by thousands of seconds: thus, these 'dynamic precursors' allow one to predict the gel failure well before the appearance of any rheological signature. The length scale dependence of the dynamics associated to these rearrangements is reminiscent of Zimm dynamics in polymers. The second regime is followed by a tertiary creep regime, where failure precursors are no longer observed, but during which the material, weakened by the strong plastic activity occurred during the secondary creep, increases its deformation rate, until a catastrophic failure occurs.

Thursday 11:50 Christiansborg

Structural fingerprints of yielding mechanisms in attractive colloidal gels

Joao Maia¹, Arman Boromand¹, and Safa Jamali²

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Core-Modified Dissipative Particle Dynamics (CM-DPD) with a modified depletion potential and full hydrodynamics description is used to study non-equilibrium properties of colloidal gels with short range attraction potentials at an intermediate volume fraction of 20% w/w under start-up shear deformation. Full structural and rheological analysis using the stress fabric tensor complemented by bond number and bond distribution evolution under flow reveals that similarly to dilute colloidal gels, flow-induced anisotropy and strain-induced stretching of bonds are present during the first yielding transition. Unlike in low volume fraction depletion gels however, a small fraction of bond dissociation is required to facilitate bond rotation at intermediate volume fractions. The strain at which structural stretching and anisotropy in bond distribution emerge coincides with the first maximum in the shear stress (first yielding transition). At higher strains, depending on flow strength, a second peak in stress signal appears which is attributed to the compaction and melting of clusters. In this work, for the first time we provide evidence that multibody hydrodynamic interactions are essential to predict the correct dynamics of depletion gels under flow, namely two-step yielding process.

Thursday 12:10 Christiansborg

Influence of particle shape on cluster rigidity and rheology of colloidal gels

Gabriele Colombo and Jan Vermant

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Colloidal gels are a class of soft materials having interesting technological applications. Many of these exploit the reversible solid to liquid transition of weakly flocculated suspensions, typical of thixotropic materials. Even tough such complex flow behavior is widespread in a number of consumer products and industrially relevant systems, the changes in microstructure underlying thixotropy remain poorly understood. Recent scaling arguments propose a dependence of the mechanical properties of gels under flow on subpopulations of rigid, isostatic clusters of closely packed particles. Such a scaling does not rely on fractal geometry or glassy dynamics, which only take into account ensemble averaged descriptors and are therefore insensitive to highly localized events, which may determine the rheological response. In this work, we intend to test and expand on these ideas of cluster rigidity, varying the packing behavior in gels by changing the particle aspect ratio slightly. The experimental approach relies on the quantitative study of the gel microstructure using high speed confocal microscopy. The link between microscopic observations and (nonlinear) rheology will be based on the orthogonal superposition rheometry technique. We also aim at clarifying the role of microstructural gel anisotropy under flow, so far neglected in current modeling efforts, whose relevance is confirmed by small strain oscillatory measurements in two dimensions. We find spectacular mechanical anisotropy in a model colloidal system for thixotropy, with a difference between elastic moduli in axial and rotational direction of up to 2 orders of magnitude.

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Symposium IR

Interfacial rheology

Organizers: Natalie Medlicott and Peter Fischer

Thursday 10:30 Fredensborg **Can a pendant drop device be used for interfacial rheology?** Jan Vermant¹ and mathias $nagel^2$

¹Department of Materials, ETH Zurich, Zurich, Switzerland; ²materials, ETH Zürich, zurich, Switzerland

The analysis of the shape of pendant drops (or sessile bubbles), has developed into an important and standard technique in the interfacial science of fluid-fluid interfaces. Such investigations are concerned with the measurement of surface tension of a liquid-air interface, interfacial tension between two liquids. However, when going to interfaces which become "com plex", due to the presence of an interfacial structure and the corresponding mechanical response, a scalar value of the surface tension no longer suffices to describe the prope- ties of the interface. In the present talks we first review approaches which generalize the Young-Laplace law in order to account for anisotropic stresses at the interface. Our discussion is based on a new fitting algorithm that uses a Chebyshev transform to describe the pendant drop interface and an inverse problem formalism with spectral method to solve for the material parameters. The accuracy of this method is then is critically evaluated.

Thursday 11:10 Fredensborg

Large area deformations of polymer monolayers using a radial through

Martina Pepicelli, Theo Tervoort, and Jan Vermant

Department of Materials, ETH Zurich, Zurich, Switzerland

In studies of the thermodynamics and mechanics of Langmuir monolayers, it is important to distinguish between different contributions to the surface stress tensor σ , namely the compressibility term $\sigma_{\alpha\beta}(\Gamma)$ rising from the thermodynamic response of the system, and the extra stresses σ_{e} , which are of rheological origin [1][2]. For purely elastic responses this separation is relatively straightforward [2][3][4]. For example, in a classical rectangular Langmuir-Pockels trough this can be obtained by positioning the Wilhelmy plate with different orientations compare to the barriers. Nevertheless, obtaining a high degree of accuracy in the plate orientation is somewhat cumbersome. Secondly, for nearly all insoluble interfaces, the Deborah number (De) typically becomes larger than one, when reaching solid-like behavior, as the relaxation time diverges, so even for the lowest compression speeds possible, with current day instruments, De>1. Therefore, rheological effects will come into play in what is invariably called a "pressure-area isotherm". In the present work, the design of the radial trough is described, which allows applying well-defined kinematics in dilatation and compression. The possibility to independently measure the dilatational modulus for different strains makes it possible to interrogate the underlying constitutive behavior. Having appropriate strain measures for compressible interfaces we can identify the different material functions. This new tool and the appropriate constitutive models enable us to correctly quantify viscoelastic effects that are sometimes interpreted as a thermodynamic property.

[1] Hermans E., Bhamla M.S., Kao P., Fuller G.G., Vermant J., Soft Matter, 2015, 11, 8048-8057. [2] Verwijlen T., Imperiali L., Vermant J., Adv. Colloid Interface Sci., 2014, 206, 428-436. [3] Cicuta P., Terentjev E.M., Eur. Phys. J. E, 2005, 16, 147-158. [4] Aumaitre E., Vella D., Cicuta P., Soft Matter 2011, 7, 2530.

Thursday 11:30 Fredensborg

Interfacial Dilatational Rheometry – a comparative study

Michael Davidson¹, Stephanie M. Kirby¹, Lynn M. Walker¹, Armon Mor², Olga Iliashevsky², and <u>Moshe Gottlieb²</u> ¹Dept. Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States; ²Chemical Engineering, Ben Gurion University, Beer Sheva 8410501, Israel

Oscillating pendant drop is a popular experimental technique for the study of interfacial rheology due to its relatively simple implementation [1]. Recently, arguments have been raised regarding the analysis of the results obtained by this technique. It has been argued that in complex interfaces such as in the presence of surfactants or macromolecules, the complex structure on the interface results in an anisotropic interfacial stress tensor which may include shear rather than purely dilatational components [2, 3]. In addition, concerns based on the aspherical shape of the droplet, the effect of curvature, Marangoni stresses, and the lack of correspondence between dilatational and shear interfacial properties have been mentioned. To explore some of these issues we have carried out a series of experiments comparing interfacial properties obtained by different techniques. In this talk we will present results obtained by oscillating pendant drop and by oscillating micro-spherical cup [4,5] for identical systems composed of a polymeric surfactant (amphiphilic block copolymer) at the water/oil interface. Shear experiments on the same systems have also been attempted and will be discussed.

1)Karbaschi M.; Lotfi, M.; Krägel, J.; Javadi, A.; Bastani, D.; R. Miller R. Curr. Opin. Colloid Interface Sci. 2014, 19, 514-519. 2)Fuller, G.G.; Vermant, J. Annu. Rev. Chem. Biomol. Eng. 2012, 3, 519-543. 3)Vermant J., Plenary talk XVII International Congress of Rheology, ICR2016, Kyoto. 4)Alvarez, N.J.; Walker, L.M.; Anna, S.L. Langmuir 2010, 26, 13310-13319. 5)Alvarez, N.J.; Walker, L.M.; Anna, S.L. Phys. Rev. E 2010, 82, 011604.

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Thursday 11:50 Fredensborg

Impact of adsorbed colloid-surfactant complexes on fluid-fluid interfaces

Lynn M. Walker¹ and Stephanie M. Kirby²

¹Dept. Chemical Engineering, Carnegie Mellon University, Pittsburgh, PA 15213, United States; ²Carnegie Mellon University, Pittsburgh, PA 15213, United States

Complexation of colloidal species (particles, proteins, macromolecules) and surfactant in bulk solution has long been used to generate complexes of different geometry, size, and surface chemistry. These complexes will have different interfacial properties than the individual components allowing for the formation of irreversibly adsorbed and elastic interfaces. The detailed control of these interfaces for optimization of interfacial properties is necessary. We are developing the knowledge and tools to have this control and also generating a characterized library of interfaces for study of phenomena like coalescence, deformation and break up of fluid-fluid interfaces. The properties (interfacial tension and interfacial rheology) of fluid-fluid interfaces with polymer-surfactant complexes and particle-surfactant complexes adsorbed will be discussed. Of specific interest is the ramifications of complex properties on these interfacial properties. Most characterization of interfaces is performed to extract isotherms, or equilibrium and steady-state behavior. For processing, the more relevant information is the transient state; knowledge of transport time scales will have a significant impact on the design of processes. One example with demonstrate the ability to alter interfacial mechanics thought nonlinear deformation of interfaces. This ability to control and generate different interfacial properties through deformation of the interface is important for processing of multicomponent layers.

Thursday 12:10 Fredensborg

The unusual interfacial shear rheology of fatty acid/alcohol Langmuir monolayers <u>Javier Tajuelo¹</u>, Francisco Ortega², Ramon G. Rubio², Eduardo Guzman³, and Miguel A. Rubio¹

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Langmuir monolayers are monomolecular-depth films formed by insoluble surfactants on fluid-fluid interfaces. Langmuir monolayers on air-water interfaces have been widely studied due to their applications in numerous industrial processes, as biological model systems, or, from a more fundamental point of view, as model systems to study the physics of two-dimensional systems.

Langmuir monolayers of fatty acids and alcohols display a very rich phase diagram [1]. While the thermodynamics of this type of 2D system has been widely investigated, much less is known about its rheology [2].

Recently we have reported on a new design of the Interfacial Shear Rheometer [3], based in magnetic tweezers [4], that extends the range of application of this technique to interfacial dynamic moduli down to 10^{-9} N/m. Moreover, it allows one to span eight orders of magnitude in interfacial dynamic moduli by playing with the probe characteristics and the optical system magnification.

We will briefly report on the new rheometer design, describing the magnetic tweezers and its fundamentals. Then we will show the results on the rheology of fatty acid and alcohol Langmuir monolayers. We will show a complete characterization of the phase space by means of rheological measurements supplemented with compressibility studies. We will show that rheology is a helpful tool to characterize the phase transitions. Finally, we will focus on the untilted S and LS phases, and we will confirm, by means of quasi-isobaric temperature sweeps, the striking thermal behavior of the viscosity of the LS phase that increases upon increasing temperature [5].

References:

[1] Kaganer, V. M. et al., Rev. Mod. Phys. **71**, 3 (1999). [2] Alonso, C. et al., J. Chem. Phys. **110**, 22185 (2006). [3] Brooks, C. F. et al., Langmuir, **5**, 2450 (1999). [4] Tajuelo, J. et al., J. Rheol, **60**, 1095 (2016). [5] Copeland, L.E. et al. J. Chem. Phys., **10**, 357, (1942).

Symposium PG

Rheology of powders and granular material

Organizers: Changquan Calvin Sun and Dietmar Schulze

Thursday 10:30 Kronborg

The influence of sweet whey powder addition on the flowability of cheese powders

Denise Felix da Silva¹, Cosima Hirschberg², Anni B. Hougaard³, and Richard Ipsen⁴

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Cheese powder properties can be affected by the use of different cheese raw materials, addition of ingredients, spray drying and storage conditions. Sweet whey powder can be added after spray drying, in a dry mixing process, or before spray drying into the cheese feed to improve physical quality. Powder flowability is related to the particle size and shape and the cohesive forces between particles. A poor flowability may result in the formation of powder overlaps in chambers, incomplete flow, or tank outlet crusting. In order to solve such issues, it is essential to understand the flow properties. The aim of this study was to evaluate cheese powder flowability with regard to addition of sweet whey powder before (co-sprayed) and after spray drying (dry mixed). A sample without sweet whey powder addition was included as control. All cheese powders were provided by Lactosan A/S. Flowability measurements were performed using a Schulze Ring Shear Tester (RST-Xs) using a preshear of 1 kPa and normal stresses of 200, 500 and 800 Pa. A Type XS-Mr shear cell was used (30 cm3). The values of major consolidation stress (MCS), unconfined yield strength (UYS) and effective angle of internal friction were obtained

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from Mohr's circles and the flow function coefficient (FFC) was calculated. Physicochemical composition, bulk density and particles size were also analysed. Control and co-sprayed cheese powders showed flowability with FFC of 2.60 and 2.55, respectively. Dry mixed samples exhibited a lower FFC (2.25±0.06) and the highest UYS (845.0±21.66 Pa), indicating a poorer flowability. No difference was found on the bulk density, fat, protein and ash content. Particle sizes surface weight mean (D[3,2]) were significantly lower in co-sprayed samples (111.17 ±7.42 µm) compared to dry mixed (150.21±3.95 µm) and control (147.95±4.57 µm) cheese powders. In conclusion, the addition of sweet whey powder in cheese powder by dry mixing causes a reduction of the powder flowability, which may consequently affect powder handling.

Thursday 10:50 Kronborg

Rheological properties of concrete: scale up from mortar paste to concrete mix with different PCI admixtures

Fabio Curto

R&D, Mapei, milano, mi 20158, Italy

For a long period concrete properties have been investigated by applicative tests. The slump test have been the only practical mean for assessment the concrete workability. The problem however, is that the slump only provides a partial description of concrete flowability. This paper shows the rheological approach in order to better define the concrete mix design. The rheology will offer the possibility to translate the concrete characterization into yield stress and plastic viscosity; the combination of the two main properties offers the possibility to fine tune the mix design. Furthermore understanding and controlling them, allows for design more economical and better performing mixes also for more complex concrete structures and concrete construction processes improvement.

Thursday 11:10 Kronborg

Dense flow around a sphere moving into a cloud of grains Antoine Seguin

Laboratoire FAST - Université Paris Sud, Orsay 91405, France

A bidimensional simulation of a sphere moving at constant velocity into a cloud of smaller spherical grains without gravity is presented with a non-smooth contact dynamics method. A dense granular "cluster" zone of about constant solid fraction builds progressively around the moving sphere until a stationary regime appears with a constant upstream cluster size that increases with the initial solid fraction of the cloud. A detailed analysis of the local strain rate and local stress fields inside the cluster reveals that, despite different spatial variations of strain and stresses, the local friction coefficient appears to depend only on the local inertial number I as well as the local solid fraction, which means that a local rheology does exist in the present non parallel flow. The key point is that the spatial variations of I inside the cluster does not depend on the sphere velocity and explore only a small range between about 0.01 and 0.1. The influence of sidewalls is then investigated on the flow and the forces.

Thursday 11:30 Kronborg Study of Rod-like Particles in Fluidized Bed by Numerical and Experimental Investigations

Vinay Mahajan and Johan T. Padding

TU Delft, Delft, The Netherlands

Non-spherical particles are often encountered in fluidized process equipment. Particle shape can significantly affect the hydrodynamics in fluidized beds. However, most of these studies focus on spherical particles while in reality, the constituent particles are seldom spherical. A coupled computational fluid dynamics (CFD) and discrete element method (DEM) approach has been extensively applied in recent years to study these flows at the particle scale. The drag force acting on a non-spherical particle can vary considerably with particle shape, orientation of the particle, Reynolds number and packing fraction. In this work, a CFD-DEM approach has been extended to model a lab scale quasi-2D fluidized bed of rod-like particles. These particles can be classified as Geldart D particles and have an aspect ratio of 4. Simulation results for the pressure drop, bed height and solid circulation patterns are compared with results from experiment. Particle velocity and orientations is studied, which provides interesting insight regarding behavior based on particle shape. Thus the capability of the CFD-DEM approach to efficiently account for global bed dynamics in fluidized bed of rod-like particle is demonstrated.

Thursday 11:50 Kronborg

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Quantitative prediction of the mu(I) rheology in 2D and 3D granular column collapse: scaling laws and quasi-static vs. inertial regimes

Rudy Valette, Stephanie Riber, Elie Hachem, and Romain Castellani

CEMEF, PSL Research University, MINES Paristech, Sophia Antipolis, France

We introduce an accurate finite element method for the computation of 2D and 3D granular collapse under gravity flows using the mu(I) rheology. This rheology is a pressure dependent viscoplastic continuum constitutive equation where the extra-stress is defined using an effective friction coefficient that increases with the inertial number. We show that this rheology can capture the two experimentally observed types of spreading and the corresponding scaling laws, and we provide an accurate sensitivity analysis to rheological constants. Finally, we underline the role of time-dependency on the spreading dynamics. These results provide complementary information to experimental literature, which reported scaling laws but did not underline a subtle but real sensitivity on the materials nature (grain friction, diameter and density). Finally, we present experimental results on granular collapse for different materials that confirm our theoretical sensitivity analysis.

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Thursday 12:10 Kronborg **Flowability of powders in laser sintering applications** <u>Peter Van Puyvelde</u>

Department of Chemical Engineering, KU Leuven, Leuven, Belgium

Selective laser sintering is a 3D printing technique to manufacture three-dimensional components from polymeric powders. In this process, a laser fuses successive cross-sections of sliced parts in a layer-wise manner. Crucial for the technique to be successful is the deposition of a uniform powder layer. Many different powder flow characterisation tools exist, ranging from a static angle of repose to more sophisticated analysis tools based on for instance fluidisation. In this work, two newly developed powder flow characterisation tools are presented and compared. The first method encompasses a modification of a commercial rheometer to accommodate powders and hence to measure powder flowability under controlled temperature conditions. The latter also indicates that effects of temperature on powder spreader set-up is presented that copies to a large extent the deformation behaviour imposed on a powder during laser sintering. Also in this case, the set-up allows to vary environmental parameters such as humidity and temperature. The two set-ups will be used to evaluate and to compare different sinter powders and can be used as a first screening method to evaluate the potential sinterability of newly developed powders.

Symposium MN

Micro and nanorheology, microfluidics

Organizers: Eric M. Furst and Anke Lindner

Thursday 10:30 Schackenborg **Wall slip of polymer gels**

Catherine Barentin¹, Marie Le Merrer¹, and Baudouin Géraud²

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Jammed polymer gels like polyacrylate-based carbopol are complex yield stress fluids widely used in applications like cosmetics or oil extraction: solid-like at rest, they become liquids under a sufficient stress. Besides, their flow properties are very dependent upon wall properties, as they can exhibit significant slip, especially under confinement like in porous rocks or in microfluidic channels. We will present wall slip measurements performed on carbopol in glass microfluidic devices, coupled to fluorescent imaging of the polymer structure. At large polymer concentration, we show that the stress-velocity relation and its dependence upon yield stress and polymer microstructure size are well predicted by the elasto hydrodynamic model developed by Meeker et al. [1] for soft spheres, despite the entanglement of polymers in carbopol. At lower concentrations, a different friction regime is evidenced, as in other yield stress fluids [2]. Finally, we discuss unsteady effects at the wall and the influence of flow history in this experimental configuration.

[1] S. P. Meeker, R. T. Bonnecaze, and M. Cloitre. Phys. Rev. Lett., 92, 198302 (2004). [2] T. Divoux, V. Lapeyre, V. Ravaine, and S. Manneville. Phys. Rev. E, 92, 060301(R) (2015).

Thursday 10:50 Schackenborg

Rheology of viscoelastic solids probed by microbubble dynamics in ultrasound

Akaki Jamburidze¹, Marco De Corato¹, Axel Huerre¹, Angelo Pommella², and Valeria Garbin¹

¹Chemical Engineering, Imperial College London, London, United Kingdom; ²Laboratorie Charles Coulomb, Universitè de Montpellier, Montpellier, France

Ultrasound-driven microbubble dynamics are central to biomedical applications, from diagnostic imaging to drug delivery and therapy. In therapeutic applications, the bubbles are typically embedded in tissue, and their dynamics are strongly affected by the viscoelastic properties of the soft solid medium. While the response to ultrasound of a microbubble in water is well understood, its behaviour in a viscoelastic material has received less attention. To model the effect of a viscoelastic medium on bubble behaviour, different constitutive equations have been combined with the equation governing bubble dynamics, the Rayleigh-Plesset equation. However, all of them require, as input, constitutive parameters which are typically measured at frequencies that are orders of magnitude smaller than those experienced in ultrasound oscillations of microbubbles (10 to 100 kHz), and their applicability in this regime is thus questionable. To address this question, we exploit ultrasound-driven oscillations of microbubbles to probe rheological properties of agarose gels at much larger frequencies than those accessible by commercial rheometers. We characterised the dynamics of isolated bubbles embedded in hydrogels by high-speed video microscopy. A modified Rayleigh-Plesset equation is used to extract rheological properties from the bubble dynamics experiments. We find that the properties of soft materials in this regime can differ significantly from those obtained at low frequency. Building on these results, we are developing a new microrheological method based on ultrasound-driven microbubbles as active probes.

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Thursday 11:10 Schackenborg

Magnetic Particle Nanorheology in Complex Fluids

Melissa Hermes, Eric Roeben, Lidia Kibkalo, and Annette M. Schmidt

Chemistry Department, Universitaet zu Koeln, Koeln, Germany

Considering the rheology of materials, one can distinguish between the macroscopic examination of the (quasi-)continuous properties of bulk materials, and microscopic probing, where characteristics of the materials are related to the microstructure of the respective sample. Micro- or nanorheology is of particulate interest for the study of soft matter and biological systems, especially when spatial mechanical properties, interfaces or particle-matrix interactions are considered. In tis novel approach of magnetic particle rheology, small particles are used as probes, allowing the time-resolved analysis of the dynamic response of the magnetic nanoprobes to oscillating magnetic fields by means of dynamic susceptibility. For this purpose, we employ poly(ethylene oxide) (PEO) aqueous solutions as model systems with well-known characteristics in terms of molecular hydrodynamic radius, entanglement length, and mesh size. As magnetic probes, we employ well-defined, magnetically blocked CoFe2O4-nanoparticles, and their Brownian relaxation in the complex fluid is investigated by means of AC susceptometry between 1 Hz and 250 kHz. The use of different theoretical models gives access to the frequency-dependent complex viscosity and mechanical moduli from complex susceptibility data.[1] In addition to the PEO model systems, we investigate the dynamic behavior of reversible networks based on terpyridine-telechelic PEO star molecules and their metal cation complexes. In order to account for size effects, we systematically vary the hydrodynamic diameter of the probe particles by attachment of a silica shell with different thickness.

[1] E. Roeben, L. Roeder, S. Teusch, M. Effertz, U. Deiters, A. Schmidt, Colloid Polym. Sci. 2014, 292, 2013-2023.

Thursday 11:30 Schackenborg

Viscoelastic properties of milk gels by passive microrheology Maxime BAZIN, Giovanni BRAMBILLA, Roland RAMSCH, Yoann LEFEUVRE, and Patrycja ADAMSKA

Formulaction, Toulouse 31200, France

Passive microrheology has become of outmost interest in recent years due to its non-invasive character. This work will present work done with Rheolaser Master©, which uses Multi Speckle Diffusing Wave Spectroscopy (DWS). A coherent laser beam is applied to the sample and multiple scattered by the scatterers (particles, droplets, fibers...) present in the sample. The interfering backscattering waves form an interference image (speckle image), which is detected by a multi-pixel detector. The scatterers' motion is directly related to the spot movement of the speckle image and can be analysed in the dynamic mode. The determination of the Mean Square Displacement (MSD) curve enables to characterize completely the viscoelastic properties of the sample. This work is focused on milk gels, such as yogurts and cheese. Rheolaser can be used as non-invasive and non-destructive technique for these delicate products. The quality of yogurt and cheese depends on many factors, such as fat content, protein content and quantity of ferment. We will show how the gel point can be easily determined in an accurate way using the TCS method [1,2]. In addition, we tried to correlate the microrheological data with the texture properties, such as creaminess, ropiness and brittleness.

[1] T. H. Larsen, E. M. Furst, Physical Review Letters, 2008, 100, 14600. [2] K. M. Schultz, E. M. Furst, Soft Matter, 2012, 8, 6198

Thursday 11:50 Schackenborg

Microrheology of monoclonal antibodies

Eric M. Furst¹, William J. Galush², Lilian L. Josephson¹, and Danielle L. Leiske²

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A key challenge encountered in the current development of therapeutic protein solutions is the need to measure their viscosity to identify stable, syringeable formulations in a large composition space. Commercially available techniques such as capillary viscometry and rotational rheometers are frequently used, but require relatively large sample volumes. This sample size requirement restricts the number of rheological measurements in the early development stage when only small amounts of protein are typically available. This talk will focus on characterizing the viscosity of protein therapeutics over a wide range of compositions with a minimal amount of material. Microrheology techniques are powerful methods to study scarce biomaterials. We use multiple particle tracking (MPT) to provide a high throughput sample processing platform for protein therapeutics. This work examines the microviscosity of three IgG monoclonal antibodies and two bispecific monoclonal antibodies assembled from IgG half-antibodies over a large range of concentrations (1 - 180 mg/mL). The protein solutions exhibit Newtonian fluid behavior over a frequency range of 0.05 to 30 s-1, and do not show evidence of further microstructure development due to protein-protein association. An analysis of covariance demonstrates the high accuracy of small volume microrheology measurements. Based on the relative error between measured and tabulated viscosities, the uncertainty of viscosities derived from particle tracking is less than 2% of the true value.

Thursday 12:10 Schackenborg Food systems characterized by DWS microrheology Mathias Reufer and Andreas C. Voelker

LS Instruments AG, Fribourg 1700, Switzerland

In this presentation, we explore the potential of microrheology based on diffusing wave spectroscopy (DWS) to access the rheological properties of food in research, production, and quality control. Diffusing Wave Spectroscopy (DWS) is a modern light scattering technique that allows the quantitative measurement of microscopic motion in soft matter systems and its main application is DWS-microrheology. This technique has several advantages over mechanical rheology such as the contact-free nature and the fast and reproducible data

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acquisition. Moreover, because the sample is not mechanically deformed, many potential artefacts like non-linear behaviour, slip, shear banding, and thixotropy can be avoided. This significantly simplifies studies on aging and gelling behaviour of shear sensitive products.

We present applications of DWS-microrheology on food thickeners like xanthan and gelatine, emulsions, and dairy products. In particular, we demonstrate the ability to measure the elastic modulus G' and viscous modulus G' over a huge frequency range at acquisition times of about 3 minutes. Moreover, we show how the gel point of gelling samples can be determined with high reproducibility in a fully automated manner.

In addition, DWS microrheology allows aging and stability studies to be performed over an unlimited period of time since the samples are sealed and can be removed and remeasured whenever required. This is a significant advantage compared to a traditional mechanical rheometer since, for such kind of studies, the mechanical rheometer would either be monopolized for the entire duration of the experiment or the sample would inevitably be altered every time it is removed and reloaded on the rheometer. Combined with the fast measurement time, DWS greatly simplifies screening and quality monitoring on many samples over an extended time.

Plenary Lectures

Symposium PL

Thursday Afternoon

Thursday 13:30 Grand Ball Complex Shear banding in wormlike micelles Sandra Lerouge

Matière et Systèmes Complexes, Universite Paris Diderot, Paris, France

We report on recent progress made on flows of living polymer fluids. Such fluids have been model systems for rheological research for more than twenty years and they continue to be fascinating. Like most if not all soft matter systems, living polymers have mesoscopic structure that can be readily reorganised by a flow. Generally, this structural reorganisation feeds back on the flow itself. Such an interplay between microscopic kinetics and macroscopic kinematics often leads to the emergence of shear-induced structures associated with highly nonlinear rheological behaviours as well as new organisation of the flow field. The shear banding phenomenon where the flow splits into domains bearing different shear rates is the prototypical example of such a flow/structure coupling. It has been observed in a wide range of complex systems but has been very intensively studied in wormlike micelles. In recent years, various tools have been developed to probe locally the flow properties and to provide a two-dimensional description of the flow. In this context, we will discuss the different time scales involved in the kinetics of formation of the shear banding flow following step shear rate and step shear stress. At long times, we will show that the coupling between the flow and the shear-induced structures leads to additional complexity in the flow dynamics due to the emergence of elastic instabilities on top of the shear banding flow. Such a phenomenology is not restricted to simple shear flow but can also be observed using other experimental protocols such as LAOS. The impact of such secondary flow instabilities on structural characterizations will also be discussed. Finally, we will show that elastic and inertio-elastic instabilities are also likely to develop on top of shear-thickening or shear-thinning wormlike micelles.

Symposium SC

Suspensions and colloids

Organizers: Norbert Willenbacher and Philippe Coussot

Thursday 15:00 Grand Ball

The role of attractive interactions on shear thinning in non-Brownian fiber suspensions

Pavel Kuzhir, Nahed-Sihem Bounoua, and Elisabeth Lemaire

Laboratory of Condensed Matter Physics, University of Nice, Nice 06100, France

This work is focused on shear thinning behavior of suspensions of rigid non-Brownian fibers dispersed in a Newtonian liquid. The work consists in developing a new theoretical model and conducting accurate experimental measurements. The shear thinning is expected to be caused by adhesive interactions between fibers. Experiments on polyamide (PA) fibers (present work) and carbon nanotube (CNT) suspensions [Khalkhal et al., J. Rheol. 55, 153-175 (2011)] have revealed the following features: (a) the flow curves exhibit a pronounced pseudo-plastic behavior interpreted in terms of the progressive aggregate destruction at the increasing shear rate; (b) the enhancement of the shear thinning with an increasing particle volume fraction is observed and explained by an increase of the strength of effective interactions between particles, as their concentration increases; (c) a weak yield stress of the PA fiber suspensions is detected in a controlled-stress mode and explained by the liquid-solid transition as the concentration of aggregates (constituted by fibers) approaches the close packing limit; (d) the shear thinning is much stronger in CNT suspensions because the adhesive interactions play a more important role between nano-sized CNT particles than between micron-sized PA fibers. A theoretical model considering the coexistence of transient aggregates with free non-aggregated fibers has been developed. The model allows viscosity calculations in terms of the aggregation parameter - the ratio of adhesive to hydrodynamic forces. It captures qualitatively the above-mentioned shear thinning behaviors and fits reasonably well to the experimental data on both PA fiber and CNT suspensions.

Thursday 15:20 Grand Ball

Shear-thinning of non-colloidal suspensions: numerical and experimental results

<u>Adolfo Vazquez-Quesada</u>¹, Arif Mahmud², Shao Cong Dai², Roger I. Tanner², and Marco Ellero¹ ¹Zienkiewicz Centre for Computational Engineering, Swansea University, Swansea SA1 8EN, United Kingdom; ²School of Aerospace and Mechanical Engineering, Sydney University, Sydney NSW 2006, Australia

Shear-thinning of particle suspensions, although being relatively well understood in Brownian colloidal systems, has also been reported in experiments with Brownian-less non-colloidal particles at high volume fractions interacting with nominally Newtonian matrices [1-3]. Despite that this phenomenon has been known for a long time the origin of non-colloidal shear-thinning is still theoretically puzzling and

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difficult to reproduce by numerical simulations where typically opposed shear-thickening is observed instead [4]. By proposing a non-Newtonian model of inter-particle lubrication forces, we show that *hidden shear-thinning effects* of the suspending medium, i.e. occurring at localized shear rates orders of magnitude larger than the range investigated experimentally, can eventually produce significant shearthinning of the overall suspension at the much smaller macroscopic shear rates explored in the experiment [5].

Numerical results will be presented and compared directly with recent experimental data for 40% volume fraction non-colloidal suspensions with different matrices, i.e. polydimethylsiloxane (silicone oils) and a glycerine/water mixture, where mild shear-thinning was always observed, followed by a downturn of the viscosity at larger shear rates [6].

- [1] F. GadalaMaria and A. Acrivos, Journal of Rheology 24, 700 (1980).
- [2] Zarraga, I. E., D. A. Hill, and D. T. Leighton, Jr., J. Rheol. 44, 185-220 (2000).
- [3] S.C. Dai, E. Bertevas, F.Z. Qi, R.I. Tanner, Journal of Rheology 57 (2), 493-510 (2013).
- [4] A. Vazquez-Quesada, M. Ellero, J. Non-Newt. Fluid Mech, 233, 37-47 (2016).
- [5] A. Vazquez-Quesada, R.I. Tanner, M. Ellero, Phys. Rev. Lett, 117 (10), 108001 (2016).
- [6] A. Mahmud, S. Dai, A. Vazquez-Quesada, M. Ellero, R. I. Tanner, in preparation (2016).

Thursday 15:40 Grand Ball

Fibre kinematics in dilute fibre Suspension with non-Newtonian suspending fluid

Tanguy Laurencin¹, <u>Patrice Laure</u>², Laurent Orgéas³, Pierre J. Dumont⁴, and Luisa Silva⁵

¹3SR Lab, Univ. Grenoble Alpes, Grenoble, France; ²CEMEF, MINES ParisTech, PSL - Research University, Sophia Antipolis, France; ³Laboratoire 3SR, Univ. Grenoble Alpes, Grenoble, France; ⁴LaMCoS, INSA, VILLEURBANNE F69621, France; ⁵High Performance Computing Institute, Ecole Centrale de Nantes, Nnates 44321, France

The mechanical properties of short fibre-reinforced polymer composite largely depend on the fibre orientation which drastically changes during the forming of composites. To analyse the flow-induced microstructures changes, we have performed three different approaches: firstly 3D in situ compression experiments using model non-Newtonian dilute fibre suspensions are performed; secondly finite element computations are made; finally the dumbbell model is checked and compared with the two first approaches. The chosen geometry induces a squeeze flow and allows to study fibre motion under elongational flow. The experiments were imaged by fast X-ray microtomography and the finite element computations are made on the same geometry by using a Eulerian multi-domain approach. Both experimental and numerical kinematics of fibres were compared to the predictions of Jeffery's model. In most cases, Jeffery's equation agrees well with the experimental and numerical data. Therefore, the non-Newtonian (power law) behavior of suspending fluid does not change the fiber motion for dilute and semi-dilute suspensions. However, for some fibres closed to compression platens, deviations between the experimental and numerical results from the theoretical predictions were observed. Adopting the dumbbell approach to modelled fibre kinematic [
bird87>] and pursuing the work of Binetruy and al. [
binetruy15>] and Perez et al. [prez16>], an extension of Jeffery classical model is proposed to take into account for confinement effect under squeeze flow with perfect slip condition.

Symposium NF

Non-Newtonian fluid mechanics and fluid instabilities

Organizers: Natalie Germann and Suzanne Fielding

Thursday 15:00 Amalienborg

A new constitutive model for time-dependent fluids

Tainan G. Santos and Cezar Otaviano R. Negrao

PPGEM, Federal University of Technology-Parana, Curitiba, Parana 81280-340, Brazil

Many fluids found in our daily lives and in industry are time-dependent, such as, daily care products, coatings, paints, drilling muds, starches, different kind of gels, suspensions, polymer solutions, polymer melts, ketchup, mayonnaise, canned baby foods, grease, melts, etc. These fluids response varies with time even for a constant imposed shear rate or stress. The flow behavior of these kind of fluids is quite important either for industrial applications (eg. What is the pumping pressure necessary to move a fluid from place to place?) or for our everyday life use (eg. How easy is it to push toothpastes from customer tubes?). Some of these fluids are classified as viscoelastic because elasticity is responsible for time-dependency and some others are said to be thixotropic or anti-thixotropic (rheopetic) as the change on the material structure causes its time response. The response of some other materials can be even more complex as they encompass viscoelasticity and change of the material structure. In the current work, a general model to predict the behavior of time-dependent fluids is proposed. This easy-to-understand and -to-fit model can be applied to either thixotropic or anti-thixotropic fluids and is a function of both load (either stress or shear) and time-dependent properties. The time-dependent materials dealt in this work are those in which an equilibrium is reached within an observable time after a constant load (stress or shear rate) is applied. This model, however, is not based on a structure parameter but rather, on time-dependent properties computed from a kinetic equation derived from a non-equilibrium condition. An elastoviscoplastic constitutive equation based on the Jeffrey's model is used to exemplify the model potential. As shown, the model can represent either yield stress or non-yield stress fluids and can predict shear banding, linear viscoelasticity and the onset of non-linear viscoelasticity.

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Thursday 15:20 Amalienborg

Rheology of irreversible time-dependent materials

Flavio H. Marchesini and Paulo R. de Souza Mendes

Department of Mechanical Engineering, Pontifícia Universidade Católica do Rio de Janeiro, Rio de Janeiro, RJ 22453 900, Brazil

In this work, the time-dependent rheological behavior of materials undergoing an irreversible process is investigated. A recently proposed thixotropic elasto-viscoplastic model (de Souza Mendes, Soft Matter, 2011, 7, 2471-2483) is modified to account for irreversible effects, which are either due to chemical reactions or shear degradation. The model is employed in step-change flows in shear rate and shear stress, and the predictions of the model are compared to experimental data available. The results show that the model is able to predict all kinds of transient behavior observed experimentally.

Thursday 15:40 Amalienborg

Rayleigh-Bénard convection for thermodependent shear-thinning fluids : secondary instabilities <u>Thomas Varé</u>, Mondher Bouteraa, Cherif Nouar, and Christel Métivier

CNRS, LEMTA UMR 7563 CNRS Université de Lorraine, Vandoeuvre-Lès-Nancy 54504, France

A linear and weakly non-linear analysis of natural convection of thermodependent shear-thinning fluids between two horizontal plates heated from below is performed. On one hand, we examine the influence of the nonlinear variations of viscosity with the temperature and with the shear-rate on the nature of the pattern wich emerges at the onset of convection. On the other hand, we investigate the impact of the shear-thinning behavior on secondary instabilities and on the range of stable wavenumbers of the preferred planform at threshold by using a set of coupled Ginzburg-Landau equations. In this study, perfectly conducting rigid slabs of infinite horizontal extent are considered. A Carreau model is used to describe the shear-thinning behavior of the fluid and the viscosity is assumed to vary with the temperature according to an exponentiel law. It is shown that (i) beyond a critical value of the ratio r_c of the viscosities between top and bottom slabs, squares are the preferred patterns at threshold and (ii) r_c increases with increasing shear thinning effects. Below r_c , there is a competition between rolls and hexagonal patterns. The range of ε (distance to the threshold) where rolls and hexagons are both stable is determined. It is shown that shear-thinning effects reduce significantly the extent of the bistability domain. Afterwards, the stability of these convective patterns is investigated. We clearly show the influence of the shear-thinning behavior on the range of stable wavenumbers. Globally, the range of stable wavenumbers increases with shear-thinning behavior for rolls and decreases for hexagons. For squares, when $r>r_c$, contrary to the Newtonian case, the « rectangular instability» is not always the mechanism which controls the range of stable wavenumbers.

Symposium GS

Gels and self-assembled systems

Organizers: Moshe Gottlieb and Henning H. Winter

Thursday 15:00 Christiansborg

Mechanics of active microtubule gels: can confinement determine elasticity?

<u>Claudia Dessi¹</u>, Daniel Blair¹, Daniel Chen², and Zvonimir Dogic²

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A rheological characterization of the viscoelastic properties of active microtubule based biopolymer gels is presented. Passive in-vitro biopolymer networks have been intensively characterized using bulk- and micro-rheology. However, active networks remain largely unexplored. Using stabilized microtubules, kinesin motor proteins, and adenosine triphosphate (ATP), we explored the dynamic viscoelastic transition from active to passive states of a unique class of biologically derived extensile active materials. By means of our coupled confocal-microscopy rheometer platform (con-rheo) we directly determine the bulk network response while simultaneously quantifying the microscopic dynamics based on the activity magnitude as driven-force. Our preliminary results indicate that these materials may be simply viscous in the active state despite the existence of long-lived spanning filaments. However, we observe a clear transition to elastic behavior that occurs as the magnitude of the activity is gradually reduced in time. We will discuss how the magnitude and the nature of active-to-passive dynamics transition depends on the geometry confinement. This is related to the observed different structural arrangement due to different fluid dynamics regime.

GS24

Thursday 15:20 Christiansborg

Effect of ohmic heating treatment on rheological and textural properties of acid milk gels

<u>Noemi Caruggi</u>¹, Mara Lucisano², Aberham Hailu Feyissa³, Saeed Rahimi Yazdi⁴, Mohammad Ali Hesarinejad⁵, and Mohammad Amin Mohammadifar⁶

¹Department of Food, Environmental and Nutritional Sciences, Università degli Studi di Milano, Milan, Italy; ²Department of Food, Environmental and Nutritional Science, Università degli Studi di Milano, Milan, Italy; ³Research Group for Food Production Engineering, National Food Institute, Technical University of Denmark, Lyngby, Denmark; ⁴Food Chemistry, Arla Innovation Center, Brabrand, Denmark; ⁵Food Science and Technology Department, Ferdowsi University of Mashhad, Mashhad, Iran; ⁶Research Group for Food Production Engineering, National Foo, Technical University of Denmark, Copenhagen, Denmark

Heat treatment is commonly applied in the manufacturing of yogurt to pasteurize it and to change the milk composition properties to improve the quality of yogurt. Ohmic heating is an alternative fast heating method for food products in which heat is internally generated within food ingredients by the passage of alternating electric current. The scope of this study is assessing the effects of ohmic heating thermal treatment on rheological and textural properties of acid milk gels formed by the hydrolysis of glucono-d-lactone. The response surface methodology (RSM) was used to find the optimal preheat treatment process condition for acid milk gels manufacturing. Gels were formed from raw milk, which had been ohmically heated at different voltage gradients (20-210 V/cm) from 20 °C to temperatures of 45-90 °C for different holding times (2-30 min). The rheological properties of these gels were determined using dynamic low-amplitude oscillation in the Thermo Scientific(tm) Haake Mars II Rheometer. The large deformation properties were studied using a Texture Analyzer XT. Plus (Stable Micro Systems Ltd. UK). Effect of ohmic heating on pH and time of gelation onset, rate of gelation and structure strength of the final gel were determined , optimized and results were compared to those of conventional preheating at 90 °C for 30 min.

Thursday 15:40 Christiansborg

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Fabrication and characterization of gels with optimum stiffness and syneresis from Lathyrus sativa protein isolate

<u>Mohammad Ali Hesarinejad</u>¹, Arash Koocheki², Seyed Mohammad Ali Razavi³, and Mohammad Amin Mohammadifar⁴ ¹Food Science and Technology Department, Ferdowsi University of Mashhad, Mashhad, Iran; ²Food Science and Technology Department, Ferdowsi University of Mashhad, Mashhad, Iran; ³Food Science and Technology Department, Ferdowsi University of Mashhad, Mashhad, Iran; ⁴Research Group for Food Production Engineering, National Foo, Technical University of Denmark, Copenhagen, Denmark

Meat consumption is inconsistently associated with the development of coronary heart disease, stroke, and diabetes mellitus, limiting quantitative recommendations for consumption levels. Plant protein foods can serve as a complete and well-balanced source of amino acids for meeting human physiological requirements without causing these diseases. Protein gelation is important to obtain desirable sensory properties and textural structures in foods. Gelation phenomenon requires a driving force to unfold the native protein structure, followed by an aggregation retaining a certain degree of order in the matrix formed by the association between protein strands. Protein gelation has been traditionally achieved by heating, but some physical and chemical processes form protein gels in an analogous way to heat-induction. The characteristics of each gel are different and dependent upon factors like protein concentration, ionic strength and/or enzyme level. Response surface methodology was employed to evaluate the influence of 3 independent variables including protein concentration, TG, and CaCl2 at 3 variation levels on the tan d (-), stiffness (N/m), syneresis (%) and turbidity (Å). The experiments were designed based on Central composite Face Center Design to obtain maximum stiffness with minimum syneresis, tan ?? and turbidity for the gels. The results indicated that Lathyrus sativa Protein Isolate (LSPI) could be used as a substitute for meat protein or as a nutritious and functional additive that plays an important role, similar to previous experience with soy protein. According to the results, the optimum condition for producing LSPI gels had significant influence on tan d, stiffness, syneresis and turbidity. Applying desirability function method, optimum operating conditions were found to be protein content of 10.39%, CaCl2 concentration of 0.60 mM, and TGase: 41.73U.g-1. At this optimum point, stiffness, turbidity, synersis and tan d were found to be 184.33(N/m), 0.77 (Å), 0.33 (%) and 0.14, respectively.

Symposium IR

Interfacial rheology

Organizers: Natalie Medlicott and Peter Fischer

Thursday 15:00 Fredensborg

Microfoams: a possible model to investigate surface rheology

Vincent Miralles¹, Emmanuelle Rio², Isabelle Cantat³, and <u>Marie-Caroline Jullien¹</u> ¹ESPCI, Paris, France; ²Université Paris Sud, Orsay, France; ³Université de Rennes 1, Rennes, France

In this presentation, we show that a thermocapillary stress induces a surface flow which can be sufficient to counteract the bulk gravity drainage, i.e. it is possible to stop, or even reverse, the drainage of a liquid foam. We report experiments using either a soluble (SDS) or poorly soluble (DOH) surfactant in a model system, a 2D microfoam, in which the full geometry of the liquid phase is known, leading a priori to accessible modelling. In the former case, surface rheology can be disregarded and a model considering mass conservation allows recovering the experimental results. In the later case, the boundary condition includes Gibbs elasticity (non homogeneous surface concentration of surfactant) and both shear and dilational surface viscosities. In this case, investigating surfactant transport mechanisms

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could not allow extracting a dominant contribution leading to the conclusion that all surface rheology properties have to be considered. However, it is shown that the different contributions (Gibbs elasticity and surface viscosities) depend in diverse ways on the geometrical properties of the foam (radius of the bubbles and Plateau border cross-section). As all the geometrical parameters of the foam are set in microfluidic experiments, we believe this experiment being useful to surface rheology investigations.

Thursday 15:20 Fredensborg

The dynamics of wet two-dimensional foams: a driven bubble in a straight channel

<u>Denny Vitasari¹</u> and Simon J. Cox²

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Aqueous foams [1] flowing through microfluidic channels have many technological applications, ranging from medical, pharmaceutical, biological fields [2] as well as oil recovery and soil remediation [3]. Control of these systems is largely driven by the geometry of the foam and the geometry of the channel, and so mathematical modelling of the situation must move beyond the quasi-static models of the dynamics of dry foams that have been used, albeit successfully, in the past, to capture how the deformation of the foam depends on its flow-rate and liquid content. We describe the extension of a "viscous froth" model to the dynamics of a wet foam in Hele-Shaw cell. The two-dimensional model includes the friction experienced by the soap films as they are dragged along the cell walls, while retaining accurate geometrical information. To explore the consequences of changing the liquid content in this situation, we consider a simple foam geometry known as a bubble lens: a bubble partially filling a narrow, straight channel with a single film spanning the gap between the bubble and the opposite wall. The triple vertices of this structure are decorated with Plateau borders whose area determines the liquid fraction of the foam. We derive new expressions to allow the pressure in the Plateau borders to be calculated, and determine numerically the range of driving velocities. For higher velocities, the spanning film moves so quickly that it leaves the bubble behind, a situation to be avoided in industrial applications. [1] I. Cantat et al., Foams: structure and dynamics. Oxford University Press, Oxford, 2013. [2] W. Drenckhan et al., Coll. Surf A, 263:52-64, 2005. [3] S.A. Jones et al., Phys. Fluids, 25:063101, 2013.

Thursday 15:40 Fredensborg

Sliding viscoelastic drops

Haonan Xu¹, Andrew Clarke², Jonathan P. Rothstein³, and Robert J. Poole¹ ¹University of Liverpool, Liverpool L69 3GH, United Kingdom; ²Schlumberger Gould Research, Cambridge CB3 0EL, United Kingdom; ³Department Of Mechanical And Industrial Engineering, University Of Massachusetts Amherst, Amherst, MA 01003-2210, United States

We study the sliding of drops of a dilute elastic liquid with a constant-viscosity (~285 mPa.s), so-called Boger fluids, on various surfaces caused by sudden surface inclination. For smooth or roughened hydrophilic surfaces, such as glass, acrylic or polycarbonate, there are minor differences between these elastic liquids and a Newtonian comparator fluid. In contrast for embossed PTFE superhydrophobic surfaces, profound differences are observed: the elastic drops slide at a significantly reduced rate (~50% and ~ 85% for the low and highly elastic fluids respectively) and complex branch-like patterns, beads-on-a-string-like phenomenon, are left on the surface. The Bond number of the sliding drops was varied from 0.8 to 2 by controlling the inclined angle and drop volume. The reduced velocities of the sliding drops can be understood via microscopy images which reveals this phenomenon is due to the combination of micro-scale surface structure and the hydrophobic nature of the surface. On these micro-scales, the local strain rates are sufficient to extend the polymer chains which remain attached on the surface, locally increasing the extensional viscosity of the solution, retarding the drop and leaving behind striking branch-like structures on much larger scales. In addition to the interesting pattern formations observed here, these results may have significant technological applications as many practical coating flows fluids are viscoelastic, as are many biological liquids.

Symposium PG

Rheology of powders and granular material

Organizers: Changquan Calvin Sun and Dietmar Schulze

Thursday 15:00 Kronborg

PG16

Can we work out Janssen equation parameters and stress dependence of the bulk density at low stress values during a simple uniaxial compression test?

Dino Ferri

Polymer Characterization, Versalis spa, Mantova 46100, Italy

Powder compression is largely used in many industrial applications. This unit operation in mechanical process engineering is often preliminar to subsequent shearing to test the flowability of the powder. The pressure profile of a granular solid column in a cylindrical container is well described using the well-known Janssen equation, which can be used even when a surcharge stress is applied on the top of the column. One of the drawbacks of this equation is the assumption of a constant bulk density. The significant pressure developed during compression leads to experimental evidences suggesting that the hypothesis of a constant density cannot be applied anymore. One of these effects is the column height dependence of the measured "average density". An approach is proposed in which a linear dependence of the

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bulk density on the stress is assumed (low stress values) and Janssen equation is consequently integrated analytically. Polyethylene powders for rotomolding were uniaxially compressed and their average bulk density values at different column heights and different stresses were modelled with the modified Janssen equation. This procedure allowed to work out reasonable values for the wall friction angle and the lateral stress ratio K in addition to the linear constitutive equation parameters describing the stress dependence of the bulk density.

Thursday 15:20 Kronborg

An insight into time - dependent consolidation with shear testing approach

<u>Cosima Hirschberg</u>¹, Jens Risbo², Changquan C. Sun³, and Jukka Rantanen¹

¹Department of Pharmacy, University of Copenhagen, Copenhagen, Denmark; ²Department of Food Sciences, University of Copenhagen, Copenhagen, Denmark; ³Department of Pharmaceutics, University of Minnesota, Minneapolis, MN, United States

Handling of powders is crucial for several industries whenever particulate systems are the starting point for any step of the whole production chain. Different industries also face similar challenges while working with different powders. Among those, flowability and cake formation during storage are the two most common challenges. The aim of this study was to explain mechanisms for powder caking by, first, inducing caking through controlling storage conditions and second, applying a consolidation pressure as a function of time. In this study, samples were stored at relative humidities of 54 %, 75 % and 95 %. The powder consolidation was performed by applying a pressure over an external consolidation bench. Powder flowability was analyzed using a ring shear tester (Schulze RST-Xs). The yield locus of the sample (without consolidation) was analyzed using a pre-shear of 2000 Pa. To analyze the flowability after consolidation for a defined time, the samples were pre-sheared in the ring shear tester and defined stress (3500 Pa) was applied externally. Afterwards, the shear cell was placed back on the ring shear tester and the shear stress under the lowest normal stress was obtained. By comparing this value with the obtained value from the flowability measurement of the same powder sample, effects of time consolidation pressure and storage induced caking could be quantified. A pharmaceutical grade lactose (spray dried a-lactose monohydrate; FlowLac 100, Meggle, Germany) was chosen as a model compound. This lactose was partially crystalline and adsorbed small amount of water (0.2 %) at a relative humidity of 90 %. A significant decrease in flowability. The preliminary data suggest that the approach adopted in this work is capable of quantifying powder caking. Thus, it can be used to investigate caking propensity of a number of fine chemical powders during storage.

Symposium MN

Micro and nanorheology, microfluidics

Organizers: Eric M. Furst and Anke Lindner

Thursday 15:00 Schackenborg

Bubble Microrheology: A new approach to extensional viscoelastic measurements

<u>Frank J. Aangenendt</u>¹, Shauvik De², Hans Kuipers², Frank Peters², Johan T. Padding², and Hans M. Wyss¹ ¹Mechanical Engineering, Eindhoven University of Technology, Eindhoven, The Netherlands; ²Chemical Engineering and Chemistry, Eindhoven University of Technology, EINDHOVEN, The Netherlands

Information on the viscoelastic response to extensional deformation of polymeric solutions and other complex fluids is crucial for understanding their behavior in a wide variety of industrial applications. While the characterization of complex fluids using simple shear experiments is well established, a complete characterization of their extensional rheological properties is still challenging. Currently, methods such as CaBER, ROJER, and microfluidics are used for this. The downside of these techniques is that fluids with low viscosity and/or short relaxation times are still hard to characterize.

Here we propose an alternative approach for measuring extensional rheological properties by using a microscopic air bubble as an extensional rheometer. We pursue this idea experimentally by submerging a single bubble in a pool of liquid and studying the dynamics of the bubble under influence of a change in hydrostatic pressure. This situation is analogous to a stress-controlled shear rheology experiment, where a time-dependent shear stress is applied to a sample and the resultant strain is measured. We test our approach on a range of polymeric fluids with different relaxation times and find that the bubble microrheology experiments provide results and trends that are indeed consistent with theoretical expectations and with previous data acquired using established methods. The concept of bubble microrheology is thus very promising. While the experimental technique is straightforward, practical improvements can still be made on the experimental setup and the data analysis, which could extend the range of investigable materials and the amount of information that can be extracted from the measurements. A chief advantage of our methodology is that it ensures the measurement of only extensional properties and that fluids with very short relaxation times can be measured. Finally, by applying a sinusoidal pressure variation instead of a pressure jump, our method could potentially be extended to oscillatory measurements.

Thursday 15:20 Schackenborg

Viscosity of protein solutions measured with dynamic light scattering using inert tracer particles

Tommy Garting and Anna Stradner

Physical Chemistry, Lund University, Lund, Sweden

Protein solutions often show a sudden viscosity increase at a certain threshold concentration, which depends on the type of protein as well as on solvent conditions. The location of this liquid-solid transition is currently hard to predict using information solely obtained from

MN22

MN23

PG17

investigations at low protein concentrations. While classical rheological experiments covering the whole concentration range provide important information, they also have drawbacks when applied to protein solutions. Many proteins unfold at the air water interface in the rheological tool and form a viscoelastic layer that precludes a correct determination of low shear properties. Moreover, relevant proteins are often available at limited quantities, and are thus not suitable for classical rheology due to the large sample volumes required. We thus use light scattering-based microrheology to extract information about the viscoelastic properties of highly concentrated protein solutions. We follow the motion of inert tracer particles embedded in small sample volumes using Dynamic Light Scattering (DLS), which allows us to extract sample viscosities at different protein concentrations. For attractive proteins that undergo a liquid-liquid phase separation, DLS-based microrheology faces an additional challenge, as these may exhibit high turbidity and strong multiple scattering due to critical scattering already significantly above the coexistence curve. DLS-based tracer microrheology then requires tracer particles with sufficiently strong scattering to dominate the protein background, and the use of a multiple scattering suppression technique such as the 3D cross correlation method is essential to avoid artefacts. We present our methodology and results on different protein systems and compare them to data obtained using classical rheology as well as other microrheology approaches. We in particular also discuss requirements on tracer particles, and the possible occurrence of artefacts due to depletion-induced tracer particle aggregation.

Thursday 15:40 Schackenborg

A Rheo-Chip platform for microfluidic rheometry of complex fluids

Alfredo Lanzaro and Peter Schurtenberger

Physical Chemistry, Department of Chemistry, Lund University, Lund SE-22100, Sweden

Microfluidic rheometry has seen a tremendous development during last decade [1]. Micro-fabricated devices offer the possibility of characterising precious fluids with available volumes of less than 1 ml (bloods, silk fibroin, biopharmaceuticals, concentrated colloidal dispersions etc.). Moreover, they can impose large and virtually inertialess rates of deformations to sample fluids. It must however be noticed that the currently available microfluidic rheometers are made by channels with integrated pressure sensors, which makes the entire device expensive and difficult to be modified and/or replaced. Also, while the development of steady shear and extensional microfluidic rheometry has already reached insightful results, there are still no available micro-fabricated devices which are capable of exploring the viscoelastic properties of complex fluids. We present a systematic rheometric characterisation of a range of high concentration materials (including colloidal suspensions and high concentration protein solutions) by means of our Rheo-Chip [1]. The device consists of microchannels with various size and geometry, a high force syringe pump, a LabVIEW-based data acquisition platform, and replaceable pressure sensors. The available data include simultaneous pressure drop and flow visualization measurements over a range of deformation rates as high as 10^5 s^(-1). The steady and transient shear viscosities are readily extracted. Also, we introduce a novel microfluidic rheometer which can impose oscillatory flow to complex fluids up to frequencies on the order of 100 Hz. It enables us exploring the behaviour of model fluids over a range of frequencies and strain amplitudes which is well above what can be achieved by conventional techniques. It is envisaged that the Rheo-chip will bring a step change to quantitative rheological characterisation of complex fluids of scientific and industrial interest, allowing for fast and high-throughput formulation screening.

[1] Yuan XF, U.S. Pat. App. No. 13/813,933.

Poster Session

Symposium PO

Poster Session

Tuesday 18:00 Marselisborg & Rosenborg

Numerical simulations of complex fluid flows within a cavity

Giovanni M. Furtado¹, Sergio Frey¹, Mônica F. Naccache², and Paulo R. de Souza Mendes²

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Some numerical results of elasto-viscoplastic fluid flows are presented in this work. The mechanical model makes use of the usual governing equations for incompressible materials, coupled with a modified Oldroyd-B equation in which the relation and retardation times, and the viscoplastic function, depend on rheology. Such a model is approximated by a three-field stabilized finite element method in terms of the extra stress, pressure and velocity fields. Simulations focus on determination of the position and shape of unyielded regions in a liddriven cavity, along with the pressure, velocity and extra stress distributions. Results indicate a strong interlace between elasticity and yield stress on yield surfaces topology.

Tuesday 18:00 Marselisborg & Rosenborg

Elasticity influence on the Coanda effect

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A straight jet emerging from a nozzle located in the very vicinity of a curved wall is deflected by the wall and will stay attached to that wall. This phenomena is called the Coanda effect, after the Romanian aerodynamicist Henri Coanda (1886 - 1972). The streamlines of the jet follow the curvature of the surface up to the separation point (SP), where the detachment of the shear layer is observed. The present study is concerned with the investigation of the elasticity influence on the Coanda effect generated by a jet in the vicinity of walls with constant curvature. The tested geometry is quasi-planar and reproduces the Hele-Shaw configuration. Direct visualizations of the flow field and PIV quantitative measurements of the velocity are obtained for low Reynolds numbers. The main aim of the paper is to relate the location of SP with the wall curvature and the elasticity number. The experiments performed with Newtonian fluids and weakly elastic solutions of PAA in water are correlated with 2D and 3D numerical solutions.

18:00 Marselisborg & Rosenborg Tuesday

Spiral vortex instability in 3D cross-slot geometries for viscoelastic fluids: a numerical study

Konstantinos Zografos¹, Noa Burshtein², Simon J. Haward², Amy Q. Shen², and Robert J. Poole¹

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In this work we numerically investigate the onset of a spiral vortex instability in a 3D cross-slot geometry of square cross section for a range of constant-viscosity viscoelastic fluids, described by the upper convected Maxwell (UCM) and the Oldroyd-B models. Previous studies considering Newtonian fluid flow in an identical configuration, report the existence of a critical Reynolds number (Re.) above which an inertial flow instability occurs [1], where the steady symmetric flow is replaced by a steady asymmetric flow with an axiallyaligned spiral vortex along the outlet channels. Here, the effects of elasticity on this vortex formation are examined by considering a range of viscoelastic fluids that are characterised by various solvent viscosity ratios, $\beta = \eta_s / (\eta_p + \eta_s)$ where η_s is the solvent viscosity and η_p is the polymer viscosity, in the range $0 \le \beta \le 0.999$.

For a range of low to moderate Weissenberg numbers, 0<Wi<1, extensive numerical simulations are performed by employing an in-house CFD code based on an implicit finite-volume method [2], to investigate the onset of flow asymmetries for various Reynolds numbers (Re). For increasing Wi we find that for all viscoelastic fluids considered, a significant reduction in Re_c occurs. We observe that as β decreases, the equivalent Re. in which the flow becomes asymmetric decreases. This is in gualitative agreement with the experimentally observed behaviour. Interestingly, for very small polymer concentrations (β ~1), both numerical and experimental results show a notable decrease in Re_c with increasing Wi. Such significant elastic effects at such low polymer concentrations have only previously been reported in the context of turbulent drag reduction.

[1] SJ Haward et al, Phys Rev E, 93:031101 (2016); [2] MA Alves et al, J Non-Newton Fluid Mech, 110:45 (2003).

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Tuesday 18:00 Marselisborg & Rosenborg Peristaltic mixing of Bingham fluids in a closed cavity: A numerical study

Zahra Poursharifi and Kayvan Sadeghy

School of Mechanical Engineering, University of Tehran, Tehran 11155-4563, Iran

Peristaltic motion is an efficient means for fluid transport in physiological systems. It is also the basis of peristaltic pumps used in industry for the transport of slurries and highly viscous fluids. In recent years, it is increasingly being used as an efficient tool for mixing enhancement in microsystem devices. The need for mixing small volumes of fluid without the contact of any mechanical component in miniaturized devices has highlighted the efficiency of peristaltic mixers. In the present work, the effect of a fluid's yield stress on the performance of the peristaltic mixing in a closed cavity is numerically simulated. The flow domain is a closed-ended rectangular cavity with the bottom wall vibrating generating a peristaltic wave. A multiple-relaxation-time Lattice Boltzmann code has been developed to study the flow behaviour in the cavity. The bi-viscosity model is utilized to simulate the Bingham fluid. Effect of yield stress has been investigated on the velocity profile variations and the flow streamline pattern. The results indicate that the yield stress has a non-trivial effect on the variation of velocity profiles which is related to the plug morphology. In order to quantify the mixing efficiency we have relied on the mean drift parameter which is a criterion based on the spatial-averaged value of the mass transport velocity representing the gross advective strength of the flow field. Based on the results obtained for the mean drift parameter it is found that when dealing with small-amplitude waves, the yield stress improves the mixing performance as compared with the Newtonian fluids. For waves having large amplitude, however, yield stress weakens the mixing efficiency.

Tuesday 18:00 Marselisborg & Rosenborg

Micro-annulus formation in density stable and unstable displacement

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In primary cementing of oil and gas wells drilling mud must be fully removed from the long narrow annulus and the annular space must be completely filled with cement slurry. Due to the rheology of the displaced drilling mud it is relatively common that a thin layer of this fluid is left attached to the walls - a so called micro-annulus. On setting, the cement dehydrates the micro-annulus leaving a porous dried mud channel that can allow gas to migrate. The objective of this study is to understand the formation of micro-annuli, by studying the displacement flow along a longitudinal section of the annulus. We study the thickness of residual wall layers in the density stable and unstable displacement of a Bingham fluid by a Newtonian fluid along a plane channel. For the sake of simplicity, this problem is studied computationally in two dimensions and it is assumed that fluids are miscible. The flow is scaled in terms of four dimensionless parameters: the Bingham number (B), viscosity ratio (m), and buoyancy number (χ^*). Density stable results indicate that a more effective displacement is achieved when the displacing fluid is more viscous than the displaced fluid (m<1). At larger (χ^*) and (B/m), the residual layer thins and consequently the efficiency of the displacement improves. We observed that the interface between two fluids can be one of three following forms: dispersive, spike, plug. On the other hand, by using a kinetic wave theory similar to E. Lajeunesse et al., (1999), we were also able to predict the interface by using a two-layer lubrication model, and describe it within the ($\chi^*/m,B/m$) plane. Interface classification is based on the existence and the position of shock on the interface. There is a qualitatively good agreement between the results obtained by computations and two-layer model. In the second problem, density unstable displacement, we observed efficient displacement in some cases although there is instability at the interface.

Tuesday 18:00 Marselisborg & Rosenborg

Effect of channel confinement on the steady flow of Bingham plastic fluids across a confined square cylinder

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In this work, the momentum transfer characteristics of a Bingham plastic medium over a square bar confined in a plane slit have been studied numerically. Depending upon the local stream level vis-à-vis the fluid yield stress, the flow domain is spanned by the co-existence of fluid and solid-like regions thereby making their homogenization and heating/cooling far more difficult than the simple Newtonian fluids like air and water. The nonlinear momentum equations have been solved numerically over the following ranges of conditions: Bingham number, $0.01 \le Bn \le 100$, Reynolds number, $0.1 \le Re \le 40$, and blockage ratio (ratio of side of cylinder to channel height), $\beta = 0.2, 0.3, 0.4$. The structure of the flow field is studied in detail in terms of the streamlines and morphologies of yield surfaces separating the fluid-like and solid-like regions. At the next level, the wake characteristics, surface pressure distribution on the submerged square are studied. As expected, wake size and surface pressure distribution exhibit positive dependence on Reynolds number (fluid inertia) and inverse dependence on the Bingham number (yield stress) which causes suppression of flow. Also a close inspection of the shear rate contours reveals that relatively higher shear stress levels at the corners and near the confining walls which fosters the presence of yielded regions (fluid like) near the cylinder and growing unyielded regions far away from the cylinder. Not only the Bingham number but it is also extent of confinement (blockage ratio) which contributes to the existing levels of stress and directly influences both the size of unyielded regions and variation in drag. The plots of the pressure drag and total drag coefficients show the positive dependence on Bingham number and blockage ratio and inverse dependence on Reynolds number. Finally, the present numerical results are consolidated via a simple predictive expression.

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Simulations of the elongation and retraction of a viscoelastic liquid film

Massimiliano M. Villone, Gaetano D'Avino, Daniele Tammaro, Rossana Pasquino, Ernesto Di Maio, Nino Grizzuti, and Pier Luca Maffettone

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The growth and burst of bubbles is a very fascinating phenomenon. Actually, understanding the behavior of such systems is also of scientific and application interest. When a film made of a Newtonian liquid is inflated and punctured, it is known that the hole opens with a velocity only depending on the surface tension between the liquid and the gas and on the liquid constitutive properties, i.e., density and viscosity, no matter how fast the bubble was inflated. On the contrary, when a viscoelastic liquid is considered, the deformation history of the film plays a crucial role on the hole opening dynamics. We perform a numerical analysis on how the inflation rate of a viscoelastic film influences the opening dynamics of a hole made in it, validating our results through comparison with experimental data. Then, we carry out an investigation on the effects of the complex fluid constitutive parameters, e.g., viscosity, relaxation time, shear thinning, and of the system geometry, e.g., film thickness, on the film burst.

Tuesday 18:00 Marselisborg & Rosenborg

Transition to chaotic flow of a viscoelastic fluid in a microscale flow focusing device Pierre Ballesta¹ and Manuel A. Alves²

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The transition to elastic turbulence was investigated in a microfluidic cross-shaped channel. The imposed flow is made of a central stream sheathed by two identical lateral streams. The resulting velocity field is measured using micro-particle image velocimetry (PIV). Two instabilities were shown to occur in this configuration. Firstly, above a critical flow rate a steady asymmetric flow is obtained; secondly, above a second critical flow rate a time dependent flow is observed. Further increasing the flow rate, leads to the onset of chaotic flow. To isolate the various possible sources of non-linear effects and compare with results of Newtonian fluids [1], the threshold of the instabilities is also investigated in the absence of either lateral streams or central flow (this last case is similar to [2]). We observed that all flows become time dependent for high enough flow rates, and we compare the onset of these instabilities to those obtained for the flow focusing device.

Bibliography: [1] M. S. N. Oliveira, F. T. Pinho and M. A. Alves, "Divergent streamlines and free vortices in Newtonian fluid flows in microfluidic flow-focusing devices," J. Fluid Mech., vol. 711, pp. 171-191, 2012. [2] A. Varshney, E. Afik, Y. Kaplan and V. Steinberg, "Oscillatory elastic instabilities in an extensional viscoelastic flow," Soft Matter, vol. 12, pp. 2186-2191, 2016.

Tuesday 18:00 Marselisborg & Rosenborg

Numerical simulation of rod-climbling viscoelastic fluid flow

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In this work we study the rotating-rod-driven flow, i.e., a rotating rod inserted into a container with a viscoelastic fluid, also known as the Weissenberg or Rod-Climbing effect. The Weissenberg effect is a classic problem in non-Newtonian Fluid Mechanics and one of many extravagant effects observed when dealing with viscoelastic fluids, for which many peculiar behaviours can be observed. It was studied in detail experimentally in the last century by an extense number of authors. These authors focused mainly on the primary states at low rod rotation rates. At higher rotation rates the flow transition to time dependent states, which are examined numerically in detail in this work. The simulations were performed with a solver based on finite difference schemes using the projection method to solve the governing equations of viscoelastic two-phase flows. The interface between the fluids is approximated using the classical volume-of-fluid interface reconstruction algorithm, and a second-order operator-split method is used to solve the advection equation. Several viscoelastic models can be used to represent the rheological properties of the (multi)-fluid phases, employing appropriate matrix reformulations for the conformation tensor. The results show a good agreement with numeric and experimental data from the literature, indicating that the proposed solver is capable to correctly simulate the multi-phase flows of viscoelastic fluids. Furthermore, above a critical value of the Weissenberg number, we were able to observe the onset of elastic instabilities driven by the combination of elastic stresses, interface curvature and secondary flows, that, as far as we are aware, have not been reported by previous numerical studies, confirming the enhanced capabilities of the new developed solver.

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Natural convection in Bingham plastic fluids from two heated horizontal cylinders in a square enclosure Lubhani Mishra and Raj P. Chhabra

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Laminar natural convection has been numerically investigated from two identical, vertically-aligned cylinders in a square enclosure filled with a Bingham plastic fluid. The coupled governing differential equations, namely, continuity, momentum and energy have been solved for the buoyancy-induced convection using the finite element method to elucidate the effect of the relevant dimensionless parameters, i.e., Rayleigh number (*Ra*), Prandtl number (*Pr*) and Bingham number (*Bn*) over the following ranges of conditions: $10^4 = Ra = 10^6$; 10 = Pr = 100 and $0.01 = Bn = Bn_{max}$ for a fixed geometry of the system, namely, the center-to-center gap between the two cylinders and blockage

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ratio (cylinder diameter/side of enclosure = 0.4). The inherent discontinuity in the Bingham plastic constitutive equation has been dealt by employing the Papanastasiou regularization. Extensive results on the velocity and temperature fields are visualized in terms of streamlines, isotherm contours and plots of the local and average Nusselt number for the aforementioned ranges of parameters. Further insights are developed by examining the iso-shear rate contours and the yield surfaces delineating the fluid-like and solid-like regions. As expected, heat transfer bears positive dependence on the Rayleigh number on account of stronger buoyancy-induced flow whereas the fluid yield stress (Bingham number) adversely influences the rate of heat transfer due to the shrinking yielded regions. It thus stands to reason that for a given geometry and fixed values of Ra and Pr, there exists a limiting Bingham number (Bn_{max}) beyond which the fluid does not yield at all and heat transfer occurs solely by conduction. Under these conditions, the average Nusselt number coincides with the corresponding conduction limit.

Keywords: Circular cylinder, Bingham plastic fluid, natural convection, finite element method.

Tuesday 18:00 Marselisborg & Rosenborg

The operation of an extrusion damper containing viscoplastic or viscoelastic materials

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We present the results of simulations, performed with a finite volume method, of the flow of a Bingham plastic and of a Phan-Thien -Tanner viscoelastic material in an extrusion damper; the latter consists of a cylindrical bore inside which a shaft with a spherical bulge oscillates sinusoidally in the axial direction. The space between the bore and the shaft is filled with the aforementioned materials, resulting in viscoplastic or viscoelastic stresses and pressure forces that resist the shaft motion leading to dissipation of the mechanical energy. The material parameters, the damper geometrical parameters, and the oscillation frequency are varied in order to examine their effect on the damper response. The latter is examined by plotting the total reaction force of the damper with respect to the shaft displacement or velocity. The study includes also the effects of wall slip; in fact, wall slip is in many cases necessary in order to abate the singularity at the intersections of the moving shaft with the stationary cylinder, bounding the force on the shaft to finite values. The behaviour of the damper depends on the relative importance of the viscous, inertial, and plastic or elastic character of the flow. When viscosity is dominant, the force is a function of the shaft velocity only, exhibiting a linear or shear-thinning relationship, depending on the fluid. On the other hand, inertia tends to introduce hysteresis in the force-velocity graph, causing greater forces during the acceleration phase of the shaft than during the deceleration phase. Elasticity is also observed to introduce hysteresis, but in the opposite sense than inertia. Plasticity tends to make the force constant, weakening its dependence on the shaft velocity. The role of the bulge is to increase the reaction force by creating a constriction where the fluid has to be pushed through. This locally increases the shear stresses, but the main mechanism responsible for the force rise is found to be the development of a pressure gradient across the bulg

Tuesday 18:00 Marselisborg & Rosenborg

Numerical simulation of planar extrudate swell of non-Newtonian fluids Raphaël Comminal, Jesper H. Hattel, and Jon Spangenberg

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This paper presents numerical predictions of the planar extrudate swell of non-Newtonian fluids exiting a slit channel. Both inelastic generalized Newtonian fluid and differential viscoelastic constitutive models are used to investigate the effects of shear-thinning, yield stress and viscoelasticity. The flow inside the channel is assumed to be fully-developed, with no-slip boundary condition at the walls. A two-dimensional finite-volume flow solver has been implemented to solve this problem. The conservation laws are solved for the streamfunction, that is a vector potential of the velocity. The streamfunction flow formulation enforces by construction the mass conservation. Moreover, it eliminates the pressure unknowns from the equations of motion. The streamfunction formulation is particularly advantageous in the case of planar flows, where the velocity is solely defined by a scalar streamfunction; the two other components of the vector potential have trivial solutions. The differential viscoelastic constitutive model are solved with the log-conformation representation, which automatically enforces the positive-definiteness of the conformation tensor. It also provides a more accurate representation of the stress gradients in exponential stress profiles. Hence, the log-conformation representation enhances the numerical stability of the viscoelastic flow solver. The combination of these two methods with implicit time-stepping and successive substitution iterations shows good convergence properties. The free-surface of the liquid is tracked with the volume-of-fluid method, on a Cartesian grid. The liquid volume fraction liquid inside the control volumes are transported with a conservative unsplit geometrical advection scheme. The position of the free-surface is reconstructed with piecewise linear functions. The numerical results will show the effects of thixotropy, viscoplasticity and viscoelasticity. Potential extension of the current method to the simulation of three-dimensional will also be discussed.

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Velocity field characteristics around a bulge-like structure observed in a cavity swept by visco-elastic fluids <u>Hiroshi Suzuki</u>, Kenichiro Tanomura, Ruri Hidema, Yoshiyuki Komoda, and Kosuke Suzuki

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Velocity measurements have been performed around a bulge structure observed in a cavity swept by a visco-elastic fluid. The flow visualization in a cavity swept by a visco-elastic fluid have been investigated in order to enhance heat transfer in a compact heat exchanger. When a visco-elastic fluid is used for ribbed heat transfer surface as heat transfer media, flow penetration into a cavity occurs due to Barus effects at a sudden expanded flow path. Thus, heat transfer from the cavity bottom is enhanced in a low Reynolds number range as reported in the previous study. Through the flow visualization, a unique flow structure in a cavity was found. A flow separated from the top corner of the cavity upstream penetrates into the cavity, reverses at the middle position of the cavity, sweeps the cavity bottom, separates from the bottom again and goes away from the cavity. The separated flow forms bulge-like structure, and then is was called a bulge structure. In this study, the velocity fields around the bulge structure have been investigated by a particle image velocimetry. From this, it was found that a

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high velocity region is formed in the outside region of the cavity due to the Barus effect. The fluid supplies to the outside and then the low velocity region appears in the center line. Due to the mass continuity, the fluid supplies from the downstream region of the cavity to the upstream region. This was concluded to be the mechanism for the bulge-like structure formed in the center line of the cavity.

Tuesday 18:00 Marselisborg & Rosenborg

Effects of the contraction ratio on elastic instability of polymer solutions in micro planer abrupt contraction-expansion channels

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Department of Chemical Science and Engineering, Kobe University, Kobe, Hyogo 657-8501, Japan

Viscoelastic aqueous polymer solutions through micro planer abrupt contraction-expansion channels induce non-linear flow instabilities. A better understanding of this phenomena is useful for many industrial applications, such as, ink-jet printing, fiber spinning, improvement of micro reaction techniques. Therefore, the phenomenon is widely studied experimentally and numerically. Lip vortices and corner vortices appearing in the upper stream of contraction-expansion channels, and a transition from flows with stable vortices to unstable flows have been studied in the last decade. However, we consider there is still room for discussion which parameter is better for understanding the phenomena, such as, extensional based properties or shear based properties. In addition, polymers used in previous studies were basic and limited.

In this study, we report experimental studies of elastic instabilities of aqueous polymer solutions through micro planer abrupt contractionexpansion channels. Several channels having different contraction ratios were prepared. Sodium hyaluronate (HA-Na), polyethyleneoxide (PEO) and hydroxypropyl cellulose (HPC) were used as aqueous polymers. HA-Na is a famous biopolymer that retains full of water, PEO is flexible polymer and HPC is a rigid polymer. Vortex growth in upper stream and flow transition to elastic instabilities were analyzed to describe the dynamics of respective polymer solutions. In order to characterize the flow, we adopted the shear rate based Weissenberg number that is known in literature, and the extensional rate based Weissenberg number that is calculated by our experimental results. The analyses based on shear and extension illustrated which stresses dominate the flow behavior. Vortex growth was well illustrated by the shear rate, on the other hand, flow transition was well categorized by the extensional rate for all polymers and for all channel geometries.

Tuesday 18:00 Marselisborg & Rosenborg

Viscoelastic fluid flow simulations using the opensource $\mathbf{OpenFOAM}^{\texttt{®}}$ toolbox

Francisco Pimenta and Manuel A. Alves

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We present our recent developments to simulate viscoelastic fluid flows using the openSOAM[®] toolbox, including a detailed description of the numerical methodology.

The *rheoTool* toolbox developed is an extension of the *viscoelasticFluidFoam* solver of Favero et al. [J. non-Newt. Fluid Mech. 165 (2010) 1625], and can be used to simulate viscoelastic fluid flows using the following differential constitutive equations: upper-convected Maxwell (UCM); Oldroyd-B; White-Metzner; Phan-Thien-Tanner (PTT); Giesekus; FENE-CR; FENE-P. The constitutive equations can be solved using the extra-stress tensor or the Log-conformation tensor methodologies [J. Non-Newt. Fluid Mech. 123 (2004) 281], and the solvers are applicable to single-phase or two-phase flows. The implementation of other constitutive equations is straightforward using the OpenFOAM[®] toolbox, and the solvers developed will soon be freely available [https://github.com/fppimenta/rheoTool], including a number of examples of application.

To assess the stability and accuracy of the *rheoTool* toolbox, a number of benchmark problems were simulated numerically, including the viscoelastic flow in a 4:1 planar contraction, the flow in cross-slot and flow focusing devices, the flow past a confined cylinder and the two-phase flow in a capillary-breakup extensional rheometer. Overall, a good agreement is found in all tested cases comparing with available data, and the methodology developed is very stable, both for steady-state or time-dependent flow regimes. Different types of purely elastic flow instabilities are successfully predicted, in agreement with previous works.

Tuesday 18:00 Marselisborg & Rosenborg

Thermal fluctuations in thin film flow of polymeric liquids Andrea Scagliarini

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When a layer of fluid deposited over a solid surface is sufficiently thin, the film is prone to rupture by capillary forces, so to minimise the interfacial energy. The stability of thin films and the dewetting of solid surfaces are of great relevance for a host of natural phenomena and technological processes. Although extensively studied, the dewetting dynamics still poses severe challenges; modelling dewetting should ideally cope with its intrinsic multiscale nature, which embraces processes from the molecular level, occurring at contact lines, to the hydrodynamic scale, like capillary waves. Moreover, many applications involve the manipulation and control of thin films of complex fluids, like polymeric liquids, whose non-Newtonian character can have highly non-trivial implications. When the film thickness reaches the nanometric scales, the validity of a fully hydrodynamic description breaks down: thermal fluctuations must be accounted for, whose interplay with surface tension and fluid-substrate interaction may lead to a significantly different behaviour. Within the framework of fluctuating hydrodynamics, I will derive a stochastic lubrication equation for power-law fluids. By means of numerical solutions of such equation, I will study the stability of thin films, showing the effect of thermal noise and non-Newtonianity on the dewetting inception and long time coarsening as well as on the spectrum of capillary waves and on the growth of a nucleated hole.

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Tuesday 18:00 Marselisborg & Rosenborg

Swelling effect of polymers used as additives in lubricants

Justine Dorenge¹, Jean-François Tassin¹, Christophe Chassenieux¹, and Fanny Briand²

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Nowadays, the reduction of car fuel consumption is one of the biggest concern for oil companies. It involves among other the reduction of friction between moving parts through the improvement of lubricant properties.

A lubricant is composed of base oil and a lot of additives that are used to improve the properties of engine oils. Among this various additives, polymeric compounds are used to modify the rheological properties, more especially for limiting the decrease of viscosity with temperature. This type of additives, called Viscosity Index Improver (VII), is based on the swelling of polymer chains with temperature due to an increase of the solvent quality for the macromolecules.

The most important parameter in the lubricant formulation is the viscosity and its dependence on temperature. The aim of the work was to study the influence of recently developed families of VII additives in different base oils in order to select the most efficient type of polymer for engine lubricant uses. Various polyalkylmethacrylates were investigated to establishing the rheological properties of the solutions, namely as a function of temperature (studying dependence of intrinsic viscosity between -40°C and 150°C) and shear rate (until very high conditions like 10^7 s^{-1}). For a given base oil, the efficiency of a VII varies with its chemical structure, its molecular weight and its concentration. Then, tribological properties were investigated using standard tests with the aim to obtain an overview of the lubricant's behavior under pressure. We also considered the degradation of this kind of polymers in a representative test in order to check the performance's durability.

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Interfacial dynamics and rheology in binary compatible systems based on PVDF and PMMA Bo Lu, <u>Khalid Lamnawar</u>, and Abderrahim Maazouz

Ingénierie des Matériaux Polymères, CNRS, UMR 5223, INSA Lyon, Université de Lyon, Villeurbanne 69621, France

We present a fundamental study of interfacial dynamics and rheology in binary compatible systems based on PVDF and PMMA. Firstly, dynamic heterogeneity with composition dependence of PVDF/PMMA blends was probed a priori from segmental to global levels. Interestingly, local heterogeneity related to a nanoscale interphase was demonstrated to exist in molten blends with intermediate compositions. The interphase revealed to be derived by mutual diffusion after melting those blends, coupled with unfavourable interchain entanglements, could explain the reduced shear viscosity and speed-up relaxations. Secondly, to amplify the interfacial effects on melt flow properties, a nonlinear rheology involving shear and elongation was investigated on PVDF/PMMA bilayers with a robust diffuse interphase. The presence of a robust macroscale interphase in the bilayers greatly delayed the onset of shear-induced interfacial failure and enhanced the transient extensional viscosity despite the relatively low the entanglement density. Besides, fitting the tube model to the shear relaxation indicated a dilated tube diameter in the interphase, confirming its weak entanglement intensity due to unfavourable interchain entanglements and its readiness to flow-induced disentanglement under large external deformations. Physics of the interfacial failure was also assessed in terms of molecular rheology theories especially with convective constraint release (CCR). Overall, the diffuse interphase at both nano- and macroscale, characterized by the weak entanglement, exerted remarkable influence on the dynamics and rheology of binary systems of PMMA and PVDF. This study will guide a better understanding of the role of interphase in multilayer coextrusion process.

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Melt strengthening of poly (lactic acid) and its blends: Shear and elongation rheological investigations for forming process

Khalid Lamnawar and Abderrahim Maazouz

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The poly (lactic acid) (PLA), through its organic origin and its biodegradation properties, can be a good alternative to petroleum-based polymers. To this end, the forming process as well blown extrusion and foaming of PLA was investigated in this study as an alternative for the production of food packaging. Through this work, we present some promising routes to enhance its processing ability which presents several challenges mainly due to the poor shear and elongation properties of this biopolymer. To our knowledge, there is few work dedicated to the investigation of foaming and/or blown extrusion of PLA that involves structural, rheological and thermo-mechanical properties. Two main routes were selected: (i) the modification of its structure, rheological and thermo-mechanical properties and (ii) blending it with other ductile thermoplastic biopolymer such as the poly (butylene adipate-co-terephtalate) (PBAT) or polyamide (PA11).To achieve this objective, various formulations of PLA with multifunctionalized epoxy, nucleants and plasticizer were prepared and characterized on the basis of their linear viscoelasticity and extensional properties. The balance of chain extension and branching has also been investigated using solution viscosimetry, Steric exclusion chromatography (SEC) and rheology (Shear and elongation rheology, relaxation spectrum, Van Gurp Palmen curves...). Finally, we pushed further by characterizing both the structure and thermo-mechanical properties of PLA formulations for forming process.

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Tuesday 18:00 Marselisborg & Rosenborg Molecular weight estimation of cellulose dissolved in ionic liquids by fitting viscoelastic data with Rouse-Zimm model

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In this study, we examine molecular weight (M) estimation of cellulose in ionic liquids (ILs) by fitting dynamic viscoelastic data to Rouse-Zimm (R-Z) model. Reliability of the fitting results are judged by comparing with the data for standard polymers in which long time (LT) term was introduced to get more faultless fitting. 1-allyl-3-methylimidazolium chloride and cosmetic cotton are weighed and mixed in sample vial bottles in a nitrogen-box. The mixtures are pre-heated then dissolved at 100°C at 0.2 atm N2 atmosphere. The solutions are divided into some vials to prepare more dilute solutions for intrinsic viscosity measurements. Dynamic viscoelastic measurements for original cellulose solutions are carried out in an MCR-300 rheometer (Anton Paar). Intrinsic viscosity was obtained from zero shear viscosities measured by rheometer. Osaki et al systematically studied G* data for standard polystyrene in dilute solution by employing LT term, which can be calculated using M, intrinsic viscosity and 2 adjusting parameters, Q and P. The calculated G" with and without LT term are practically the same, while G' data in the lower frequency region can be well fitted by addition of the LT term. Therefore, we first fitted the G" data with original R-Z model by using M as adjustable parameter while others from experimental conditions. Note that our solution is in Rouse like region. By using obtained M and intrinsic viscosity, we further fitted the data to R=Z model with LT term. The fitting became excellent through all frequency region for G'. The values of Q and P are consistent with the reported values. From these results, we conclude that as long as the relaxation time can be precisely determined from the data, we can estimate M of cellulose in IL solution by the fitting method.

Tuesday 18:00 Marselisborg & Rosenborg

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Rheological characterization of molten polymer-drug dispersions as a predictive tool for pharmaceutical hot-melt extrusion processability

Jeroen Van Renterghem¹, Ruth Cardinaels², Chris Vervaet³, and Thomas De Beer⁴

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Rheological characterization of solid dispersions has predictive potential for hot melt extrusion processability because it provides information about (i) the viscosity as a function of temperature and shear rate; (ii) drug solubility in the polymer matrix and (iii) shear induced crystallization. The aim of this study was to investigate (i) the influence of drug solid state (crystalline or dissolved in the polymer matrix) on hot-melt extrusion processability and (ii) the influence of drug concentration and shear rate on polymer crystallization using rheological tests. Poly(ethylene oxide) (PEO) (100.000 g/mol) and physical mixtures (PM) containing 10-20-30-40% (w/w) ketoprofen or 10% (w/w) theophylline in PEO were rheologically characterized with a Haake Mars III Rheometer using a 20 mm parallel plate geometry. Rheological tests were performed (frequency and temperature sweeps in oscillatory shear as well as shear induced crystallization experiments) to obtain a thorough understanding of the flow behavior and crystallization of PEO-drug dispersions. Theophylline did not dissolve in PEO as the complex viscosity (Eta*) of the physical mixture increased as compared to that of neat PEO. In contrast, ketoprofen dissolved in PEO and acted as a plasticizer, decreasing Eta*. Acting as a nucleating agent, Theophylline induced the crystallization of PEO upon cooling from the melt. On the other hand, ketoprofen inhibited the crystallization upon cooling. Shear enhanced the crystallization speed of PEO for physical mixtures containing ketoprofen. Higher concentrations of ketoprofen in the physical mixture inhibited polymer crystallization. Active pharmaceutical ingredients (APIs) change the melt flow behavior of polymers. Also the polymer crystallization is altered by temperature, shear and the API's solid state (crystalline or dissolved). This is important for understanding HME processability (e.g., barrel temperature selection) and downstream processing such as injection molding (e.g., mold temperature selection).

Tuesday 18:00 Marselisborg & Rosenborg

On shear-banding and wormlike micellar system response under complex flow

<u>Michael F. Webster</u>¹, J. Esteban López-Aguilar¹, Hamid Reza Tamaddon-Jahromi¹, and Octavio Manero² ¹College of Engineering, Swansea University, Swansea SA1 8EN, United Kingdom; ²Instituto de Investigaciones en Materiales, Universidad Nacional Autónoma de México, Mexico City 04510, Mexico

This predictive study focuses on the finite volume/element modelling of shear-banded wormlike micellar material systems. In this a modified planar Couette-flow is considered, generated by a moving top-plate in a rounded-corner 4:1:4 contraction-expansion geometry. Pure-shear Couette-flow is observed in fully-developed entry-exit regions, away from the obstruction, whilst mixed shear-extensional flow arises around the contraction-zone. This offers the possibility to gather zones of pure shear-banding in the entry flow-region, and to observe corresponding system response within and beyond the complex flow zone, when exit-zone pure-shear flow-conditions are recovered. For this purpose, a revised BMP+_tp model is used to represent the response of such wormlike micellar systems under shear-banding conditions. New beneficial features to this advanced BMP+_tp model-variant are bounded extensional-viscosity response and an N_{1Shear}-upturn at high deformation-rates. Experimental evidence would indicate that, extremely polymer-concentrated micellar-fluids with non-monotonic shear-stress flow-curves, are required to generate shear-banded solutions. Ensuing flow structure is analysed at appropriately selected flow-rates through velocity, stress and streamline fields. For the (?=3)-banding-fluid, an intermediate flow-rate (Q=30) lies within the shear-banding deformation-rate range, thus providing banded-solutions; whilst the lowest flow-rate (Q=4) and highest flow-rate (Q=450), lie outside the shear-banding regime, with non-banded solutions derived accordingly. Then, for the banded (Q=30)-solution, split velocity fields in the upstream flow are recovered in the downstream fully-developed regions. Such a split velocity-field response corresponds to two or more bands, with different viscosity (structure) but constant overall shear-stress. Approaching the contraction, such

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segregated flow collapses into a unified material response. Consistently, the non-banded-fluid provides non-banded solutions at all flowrates.

Tuesday 18:00 Marselisborg & Rosenborg

Filament stretching extensional rheometer for low viscosity solutions

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Extensional rheometry has always been an experimental challenge. Past years have shown for uniaxial extensional deformations a remarkable progress with the development of the filament stretching extensional rheometer (FiSER) and lab bench instruments as the SER and EVF fixtures, or the recently introduced Vader. Still, up to now there was a lack of instrumentation to investigate lower viscous systems in uniaxial extension. The main drawback of the above techniques is the low strain rate that can be achieved. At a low strain rate, the thinning behavior of solutions with low viscosities are dominated by gravitational sagging and capillary thinning which prevents investigation with currently available instruments. While capillary break-up indexers as the CaBERs allow qualitative evaluations of such low viscous systems, it would be desirable to have an instrument that can access both, lower viscosities and higher rates in uniaxial extension.

In this paper, we would like to introduce a new, improved version of a home-built filament stretcher which can reach higher controlled constant strain rates, using synchronous servomotors coupled to a tooth-belted drive axis in combination with fast feedback control of the fluid's deformation. In addition to these higher strain rates, the new filament stretcher is equipped with a rotating top plate which creates the possibility to apply a defined shear history. This feature enables the investigation of time-dependent properties by tuning the strain and shear rate history prior to extension. Several model low viscous polymer solutions are tested to validate the new set-up.

Tuesday 18:00 Marselisborg & Rosenborg

Rheological behavior impact on bubbles motion in semi-dilute polymer solutions

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One of the most promising methods to improve oil production is Chemical Enhanced Oil Recovery based mainly on surfactants and polymer injection. The polymer is used to avoid digitations by increasing the water viscosity. However, a part of this additive is found back on surface and has a negative effect on water treatment. Induced gas flotation is an efficient technique to remove oil droplets from the produced water. It is mainly based on the air bubble and oil droplet attachment and combined rise. In EOR context, the hydrodynamics and interfacial phenomena are adversely affected and the flotation efficiency is reduced. To understand this impact, we first focus on the polymer influence and the consequences of its rheological properties on the bubble flow. Contrary to the dilute regime with Newtonian fluid and well dispersed bubbles, in the semi-dilute regime, the high molecular weight HPAM polymers create preferential ways for the rising bubbles and also stabilize a foam. At high concentrations, a jet of bubbles appears at the center of the column. This phenomenon is often attributed to only the solution elasticity while the HPAM solutions have a strong shear-thinning behavior. So, we propose to discuss the relative contributions of elasticity and shear-thinning to the bubble flow change. In parallel, we study the motion of successive bubbles formed with a capillary. The bubble size and speed are measured with a high-speed camera. The studies have been done with different polymer molecular weights and at high concentrations. To explain the results, rheological characterization of the HPAM solutions have been performed: shear (continuous and oscillatory) tests using a rotating rheometer and elongational rheometry within a hyperbolic microfluidic contraction. Our results highlight the impact of the polymer shear-thinning behavior on the bubble swarm motion: some bubbles are accelerated and then clusters appear. We also found a relation between the period of stress imposed by bubble passing and the relaxation time.

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Modeling the dynamical behavior of reinforced rubbers using a superposition approach <u>Ievgeniia Ivaneiko</u>, Vladimir Toshchevikov, Klaus Werner Stöckelhuber, Marina Saphiannikova, and Gert Heinrich *Leibniz-Institut für Polymerforschung Dresden e.V., Dresden 01069, Germany*

The main goal of our study is to develop a superposition approach for description of the viscoelastic properties of reinforced elastomers. To investigate the influence of several factors of filler surfaces on these properties, a number of rubber compounds, based on SSBR as matrix and different types of fillers, were chosen. We used fumed silica, precipitated silica in three different grades and carbon black. The master curves were constructed with a help of a shifting procedure [1] based on the time-temperature superposition principle. To fit the master curves in the whole range of frequencies over 15 decades, we develop a superposition approach, which allows extracting the characteristics of a fully localized polymer layer on the filler surface. The complex modulus of the reinforced rubber is given as a superposition of the complex moduli of the matrix and localized layer, weighted with a volume fraction of the matrix, Cm. The frequency-dependent moduli can be described using the spectrum of relaxation times which consists of four power-low regions separated by characteristic times starting from the relaxation time of a single monomer till the terminal relaxation time [2,3]. The middle regions are characterized by the bending rigidity exponent of 3/4 and by the Rouse exponent 1/2 for the matrix. In the presence of filler the Rouse-like behaviour of the free chains changes to the slowed down behaviour of the localized chains. After successful fitting procedure we can extract the thickness of a localized layer when knowing the radius of the filler particle. In our case the layer thickness is estimated to be of the order of 5 nm. Further we can predict the filler volume fraction, at which the full localization takes place. Our results suggest that the surfaces of studied fillers impose quite different localization constraints on the rubber chains.

[1] I. Ivaneiko et al., Adv.Polym.Sci, 2017, 275, 157. [2] M. Saphiannikova et al., Macromolecules, 2014, 47, 4813. [3] I. Ivaneiko et al., Polymer, 2016, 82, 356.

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Tuesday 18:00 Marselisborg & Rosenborg

The mechanism of fracture for entangled polymer liquids in extensional flow

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In uniaxial extensional flow of entangled polymer liquids, different rupture modes may happen, including necking and fracture. Malkin and Petrie [1] proposed a "master curve" dividing the flow behavior into four zones based on the stretch rate: (I) Flow zone; (II) Transition zone; (III) Rubbery zone; and (IV) Glass-like zone. The master curve shows that steady extensional flow can only be reached in Zone I where the stretch rate is very slow, while rupture happens in Zones II-IV with faster stretch rate. Furthermore, Wang et al. [2-4] reported experimental data that matches the master curve and suggested the mechanism of rupture in Zone III and IV is disentanglement and chain scission, respectively.

In this work we measure two groups of entangled polystyrene solutions. In one group the samples have the same entanglement molecular weight (Me) but different number of entanglements (Z), and in the other group the samples have the same Z but different Me. We show that in controlled filament stretching, steady extensional flow can be reached in Zones I-III, while fracture happens in Zone IV. The critical strain at fracture decreases with increasing stretch rate, which is in agreement with the master curve in Zone IV. However, with faster rate, a constant critical strain is observed, which is not shown in the original master curve. The value of the constant critical strain seems to be related to the maximum stretch ratio of the polymer chain (determined by Me), but not influenced by Z. The results are also compared with the critical strain of chemically crosslinked polymer networks.

[1] A. Ya. Malkin and C. J. S. Petrie, J. Rheol. 41, 1-25 (1997)

[2] Y. Wang and S. Wang, Rheol. Acta. 49, 1179-1185 (2010)

[3] Y. Wang and S. Wang, Macromol. 44, 5427-5435 (2011)

[4] X. Zhu and S. Wang, J. Rheol. 57, 223-248 (2013)

18:00 Marselisborg & Rosenborg PO30 Tuesdav Varying efficiency of differential constitutive equations based on either steady shear or unsteady (LAOS) characteristics

Radek Pivokonsky, Jana Zelenkova, and Petr Filip

Institute of Hydrodynamics, Acad. Sci. Czech Rep., Prague, Czech Republic

Efficiency of differential constitutive models (exponential Phan-Tien and Tanner, Giesekus, Leonov, and modified eXtended Pom-Pom) describing behaviour of a solution of poly(ethylene oxide) in dimethyl sulfoxide is evaluated in two steps. Firstly, nonlinear parameters of the models are optimized with the respect to steady shear measurements and consequently their ability to describe large amplitude oscillatory shear (LAOS) characteristics is tested. Secondly, nonlinear parameters of the models are optimized with the respect to LAOS measurements (both real and imaginary component of the stress amplitude are taken into account) and applicability of the models is tested against steady shear characteristics. In the first case, it is shown that the models are not capable of fitting the LAOS characteristics. In the second case, it is shown that optimization of nonlinear parameters is more responsible. Hence, a determination of the model parameters through LAOS measurements makes the models much more efficient. Acknowledgement: The authors wish to acknowledge the Grant Agency CR for the financial support of Grant Project No. 17-26808S.

18:00 Marselisborg & Rosenborg Tuesday **Coarse-Grained Simulations for Entangled Star Polymer Melts** Ankita Pandey and Yuichi Masubuchi

Nagoya University, Nagoya, Japan

In spite of the remarkable success of tube models, there still remains several issues for description of branch polymer dynamics. For example, the role of the spatial fluctuations and curvilinear hopping of the branch point have not been clarified yet. In the present work, we extend the multi-chain slip- spring (MCSS) model to focus on the dynamics of branch point. In the MCSS model, Rouse chains are temporally connected via slip-springs which mimics entanglement. The distinguishable feature of this model from the tube model is the motion of branch point. Although the branch point mobility has been examined via the multi-chain slip-link model, in the MCSS model the segmental dynamics is traced, and thus, re-equilibration process at the creation/destruction of entanglement is naturally considered. Comparison to the tube and the slip-link models will be discussed in terms of the branch point motion.

18:00 Marselisborg & Rosenborg Tuesday On rheology of novel (co)polyesters after UV-weathering: structure/degradability relationships

Haroutioun Askanian¹, Sophie Commereuc², Annamaria Celli³, and Vincent Verney⁴

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A novel class of aliphatic polyesters, and their derived copolyesters, have been developed. Beside their specific mechanical and thermal properties, the durability, in terms of biodegradability and photodurability, has been investigated. In particular, the polymers were submitted to natural and accelerated photo-ageing and an original methodology based on melt rheology has been applied to determine molecular changes upon UV weathering. Both scission and recombination reactions, which strongly compete as a function of the exposure time, were found to cause a strong evolution of the molecular structure. The results indicate that chemical structure and stereochemistry of the novel materials define the predominant process and the overall behaviour of the samples upon UV exposure. Moreover, the changes of the molecular structure, induced by UV irradiation, could have a significant role into the further biodegradability of the polymers.

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Therefore, while the relationships between structure and durability enable to design materials with desired well-adapted performances according to their final destination, the biodegradable character upon lifetime use is considered as really questionable and needs further studies.

Tuesday 18:00 Marselisborg & Rosenborg

Investigation of the influence of the properties of polymer solution on the properties of electrospun fibers Xiaoli Liu¹, Johanna Aho¹, Stefania G. Baldursdottir¹, Haiyan Qu², Lars Porskjær Christensen², Jukka Rantanen¹, and <u>Mingshi Yang¹</u>

¹University of Copenhagen, Copenhagen, Denmark; ²University of Southern Denmark, Copenhagen, Denmark

Micro- or nanoscale fibers have been used for biomimetic structures, such as tissue scaffolds, modern wound dressings and drug delivery carriers1. Electrospinning is a versatile, cost effective and simple process for producing micro- or nanoscale fibers by exposing polymer solution/melt to a high voltage. The aim of the study was to investigate the influence of the properties of polymer solutions on the properties of electrospun fibers, by studying polymer poly(lactic-co-glycolic acid) (PLGA) solutions in various solvents, and the corresponding properties of electrospun fibers. The PLGA (RG750) with a ratio of 75:25 of lactic acid (LA) and glycolic acid (GA) was investigated. Various solvents and solvent mixtures were tested for dissolving the polymer. Viscoelasticity and surface tension of the polymer solutions were investigated prior to the electrospinning process. Solvent screening study showed that Dimethylformamide (DMF)-tetrahydrofuran (THF) solution, and DMF-chloroform (CHL) solution provided stable cone-jet in the electrospinning process. The resulting electrospun nanofibers were characterized with respect to morphology, and mechanical properties. At the concentration range studied (i.e. 10-30% (w/v)), the PLGA solutions could be electrospun into uniform fibers when the concentration reached 30 % w/v. The polymer solutions were more elastic and had higher viscosity when DMF-CHL was used compared to DMF-THF. As a result, RG750 electrospun fibers had a larger diameter, higher stiffness, and tensile strength when they were electrospun from DMF-CHL.

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Effects of Cellulose Nanofibrils on Rheological Properties of Fresh Cement Paste and influence on Strength Properties of Hardened Cement

Fredrik W. Brodin, Berit Leinsvang, Johnny Kvakland Melbø, and Kristin Syverud

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The rheology of fresh concrete is enormously important for its applicability in various end applications. Rheology modifiers are actively used in the concrete industry to tailor the flow properties of concrete to desired values. Therefore, new types of rheology modifiers are of significant interest for this industry.Nanocellulose is a novel bio-based nanoscale material which has large possibilities within many different application areas. The nanoscale dimensions of cellulose nanofibrils (CNF), its ability to changethe rheology of suspensions and the high strength of the individual fibrils makes this material interesting for use in cement and concrete. In this study, CNF have been used as a rheology modifier in fresh cement paste. Two different types of CNFshave been added in various amounts into fresh cement paste, and rheological measurements have been conducted to investigate how CNF affects the flow properties. The results have shown that the two CNF grades have large impact on both yield stress and paste viscosity even at very low concentrations. Furthermore, flow curve data have been fitted to various rheological models to determine model parameters for this system. The rheological parameters have also been correlated to the strength properties of the hardened cement to find relations between CNF containing cement in its fluent and its hardened state.

Tuesday 18:00 Marselisborg & Rosenborg

Study of Marangoni stresses induced by clay at the interface in PMMA/PS blends

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The immiscibility of most polymers gives the possibility to control the final properties of a polymer blend by tailoring its morphology. However, this immiscibility can lead to unstable morphologies or even phase separation which results in poor physical properties. To control and stabilize the morphology over time, a compatibilizer is normally added to the blends. In the case of a droplet dispersion, the presence of the compatibilizer at the interface causes a reduction of dispersed phase size, decrease of interfacial tension, inhibition of coalescence and the presence of additional relaxation phenomenon due to Marangoni stresses. In this work, the Marangoni stress phenomenon was studied. In order to do so, three different clays: Montmorillonite, Laponite and Halloysite (organically modified or not), were used to compatibilize poly(methyl methacrylate) (PMMA) / polystyrene (PS) blends. The linear viscoelastic behavior, in particular the relaxation spectra inferred from SAOS results, were studied. The spectra displayed the relaxation time of the pure phases (PMMA and PS), the relaxation spectra of the blends to which non modified clay or Halloysite was used did not present a third relaxation time indicating that in this case the clays are not located at the interface. However, the relaxation spectra of the blends to which modified Montmorillonite and Laponite was added both displayed a Marangoni stress relaxation time evidencing the importance of surface chemistry of the compatibilizer. The comparison of Halloysite, Montmorillonite and Laponite evidenced the influence of the shape factor on the Marangoni stress.

Tuesday 18:00 Marselisborg & Rosenborg

Rheological characterization of hybrid LDPE nanocomposites containing graphite nanoplatelets <u>Danilo J. Carastan¹</u>, Roland Kádár², and Mikael Rigdahl³

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The development of polymer-based nanocomposites has become increasingly important over the years, as the addition of nanoparticles improves mechanical and functional properties at low particle loadings. In particular, graphene has become one of the most studied nanomaterials, as well as related materials, such as graphite nanoplatelets, even though dispersing and exfoliating them in a polymeric matrix remains a challenging task. One of the strategies is to produce materials containing more than one type of nanoparticle, so that they interact with each other, eventually forming self-assembling structures, with better ordered spatial arrangements. In this work, nanocomposites of low density polyethylene (LDPE) with different average molecular weights and degrees of branching were prepared by adding different nanoparticles (different nanoclays and silica nanoparticles) in combination with graphite nanoplatelets. The nanoparticles were initially dispersed in suitable solvents using a high-speed rotor-stator homogenizer, and powdered LDPE was added to the suspensions in order to form nanoparticle-coated polymer particles upon solvent evaporation. The mixtures were then melt mixed and compression molded. The samples were characterized by optical and scanning electron microscopy, and their shear rheological properties were studied in the linear viscoelastic regime. Their dynamic-mechanical properties were also tested in the solid state as a function of temperature. The results showed that for the nanocomposites in the molten state, depending on the nanoparticle combination, the storage modulus increases at low frequencies if compared to their pure nanoparticle counterparts, suggesting the formation of networks between the nanoparticle pairs. In the solid state, the moduli are more sensitive to the presence of graphite nanoplatelets than to the other nanoparticles studied.

Tuesday 18:00 Marselisborg & Rosenborg

Filled rubbers manifesting superposed nonlinear viscoelasticity

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Seeking relations for inter-conversions of viscoelastic properties of rubber materials in the nonlinear regime is a scientifically challenging and industrial important problem. In this study, we investigated the step-shear and oscillatory-shear responses of a number of vulcanized filled rubbers. We find that in both linear and nonlinear regimes the mechanical properties of filled rubbers exhibit excellent superposed rheological behavior, particularly, the damping function obtained from the time-deformation separability takes the same form as the Payne effect obtained from the frequency-strain superposition does. We will discuss the implication of this result to the recent advances of nonlinear viscoelasticity for complex rubber materials.

Tuesday 18:00 Marselisborg & Rosenborg

Nano structural rheology and the mesoscale

Eric Stellamanns¹, Daniel Weschke², and Michael Sprung³

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Structural rheology happens over multiple time and length scales, hence understanding the rheological properties of complex fluids under shear needs observation of all relevant length and time scales simultaneously. By combination of optical and x-ray scattering techniques with a stress and temperature controlled rheometer, we are able to provide insight into the complex structure of flow from the nano to the mesoscale in situ. Based on an inverted Haake MARS II rheometer, we developed a specialized set of rheo sensors that are transparent for both, high and low energy electromagnetic radiation together with a high temperature probe environment and solvent trap that allows for the x-ray beam to pass through and provides apertures for the x-ray detector together with a high resolution microscope. With this toolbox, it is now possible to examine shear and temperature induced mechanical changes in a material and directly correlate them to structural changes: 1. On the molecular scale by wide angle x-ray scattering 2. On the nano scale by small angle x-ray scattering and 3. On the mesoscale by polarisation microscopy and wide field observation. In this way, a wide range of materials can be examined, from water based biological systems or colloidal suspensions, making use of the solvent trap, to highly temperature sensitive liquid crystals or high performance polymers that melt at 300°C and above. Given the high brilliance and flux of the PETRA III synchrotron in addition to reduced background scattering and a suitable detector, we achieved a temporal resolution up to 2 kHz for x-ray scattering. At such a high spatio temporal resolution, it is possible to conduct x-ray photon correlation spectroscopy and thereby quantify the structural dynamics during shear and relaxation. The different components and function of the setup will be explained in detail and supported by the results of user as well as in-house research on the example of colloidal suspensions, liquid crystals and polymer melts.

Tuesday 18:00 Marselisborg & Rosenborg

Fibrin nanoscale packing controls its non-linear, fatigue and rupture properties

Xabel Garcia¹, Landry Seyve², Denis C D Roux¹, Benoît Polack², and <u>Francois Caton¹</u>

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Fibrin clot formation is one of the major processes leading to blood clotting. Fibrin is a biopolymer gel which constitues the scaffold of blood clots and determines their mechanical properties. While environmental factors (pH, ionic strength,...) are known to influence the polymerization and properties of fibrin, the influence of fibrinogen composition remains unexplored.

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Using Small Angle X-Ray scattering, multi wavelength spectrophotometry as well as confocal microscopy, we characterize in detail the multi-scale structure of fibrin gels made from several fibrinogen preparations. Gel filtration, dynamic light scattering, and mass spectrophotometry of the fibrinogen preparations show that fibrinogen polydispersity has the strongest influence on the multiscale structure of fibrin gels while the composition in co-purified proteins bears little influence. Indeed, fibrin fibers made from monodisperse fibrinogen are almost crystalline while those made from polydisperse fibrinogen are much less well organised.

Concerning the mechanical properties of those fibrin gels, the "crystalline" and "amorphous" gels show very significant differences, both in the non linear regime as well as in the fatigue and rupture regime.

Those results open very interesting perspectives in many fields such as tissue engineering and regeneration, as well as the understanding of the relationship between abnormal clots and cardiovascular diseases.

Tuesday 18:00 Marselisborg & Rosenborg

Evaluation of fish fillet quality by empirical, fundamental and non-destructive tests

Mohammad Amin Mohammadifar¹, Flemming Jessen², and Jacob Lercke Skytte³

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Freshness is one of the most important quality markers of fish not only due to the sensory perception, but because the absence of freshness can have serious consequences on health. Non-sensory evaluation methods in the determination of fish quality, providing more rapid and economical results. Texture analyzer (large deformation and destructive), dynamic rheological measurements (small amplitude oscillatory) and Spectral analysis and Image processing have been used as effective tools to assess fish quality. But the measured parameters have not the same power to reveal changes in fish quality. Major objective of this study was to investigate the sensitivity of empirical and fundamental rheological parameters to any changes in various parts of salmon fillet due to storage condition .Study the potential of using hyperspectral imaging technique in the spectral range of 400 - 900 nm as a rapid and non-invasive tool for assessing texture attributes of salmon fillets was the second aim of this study. Finally correlation between rheological attributes and non-invasive measurements were studied to determine if it is reliable to use them alternatively.

Tuesday 18:00 Marselisborg & Rosenborg

Investigating the viscoelastic properties of porcine bladder using dynamic mechanical analysis

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This study examines the use of dynamic mechanical analysis (DMA) for measuring the viscoelastic properties of fresh female porcine bladder samples. Knowledge of the viscoelastic properties of tissues is crucial when engineering artificial grafts and tissues. An ideal substrate for cell grafting should have similar viscoelastic properties to the tissue it is intended to replace. Porcine bladder samples were cut out in pieces 30 mm long with width 6 mm and thickness 4 mm. The samples were mounted in a DMA equipped with a film tension clamp. The sample length were 10 mm and they were subjected to a frequency sweep from 10 Hz to 0.1, recording 5 data points per decade using an amplitude of 200 μ m. The samples were measured both in the X (transversal) and Y (longitudinal) directions and the storage and loss moduli were recorded. The storage modulus of porcine bladder was relatively constant at all frequencies, 30 ± 7 kPa, while the loss modulus was constant at 6 ± 1 kPa from 0.1 to 1 Hz and then showed a sharp drop to 0 ± 2 at 10 Hz, indicating that less energy is dissipated and more energy is stored with increasing frequency (i.e. the samples become more elastic). There was no difference between the transversal and longitudinal directions. These results establish DMA as a useful tool for analyzing the viscoelastic properties of tissues. The results obtained will be used in the design and development of biomaterials intended for tissue engineering applications.

Tuesday 18:00 Marselisborg & Rosenborg PULSATING FLOW BEHAVIOR OF HUMAN BLOOD

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In this work, the rectilinear flow of human blood under a pulsating time-dependent pressure gradient is analyzed. A first approximation of the real case of blood flowing in a vein is derived and studied. The pressure gradient simulates the pumping work of the heart while the flow geometry (circular tube) is assumed rigid, smooth and cylindrical. The rheological behavior of blood with different cholesterol levels is modeled considering it as a non-newtonian shear thinning fluid exhibiting complex flow phenomena (yield stress) by using the Bautista-Manero-Puig (BMP) constitutive equation. According to the analytical solution (first order solution), a flow enhancement is predicted which represents the optimum pumping work of the heart. This work is a contribution to the understanding of the complex rheology involved in the discontinuous pressure driven flow of blood in the human body.

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Tuesday 18:00 Marselisborg & Rosenborg Large amplitude oscillatory shear and sensory profiling of Peanut butter and Tahin

Maria B. Larsen¹ and Pia I. Hedelund²

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There is a large natural variation in the raw materials used to produce Peanut butter and Tahin. In order to ensure a uniform and consistent outcome between production batches, quality parameters need to be defined. Based on products from Urtekram International A/S, physical and rheological measurements and sensory analysis, have been performed and correlated to establish cohesion between the perceived sensory sensation and the instrumental measurements. Hereby generating the information required to create a quality control program. Hence, viscosity, large amplitude oscillatory shear, particle size and descriptive sensory analysis have been applied on the different products. The results show that it is difficult to measure viscosity of the samples in the shear rate interval from 10-100 s-1, which simulates chewing. The large amplitude oscillatory shear data from strain 100-1000%, on the contrary, could be correlated to data obtained from the sensory product profile. The particle size data could be correlated to large amplitude oscillatory shear from 1-10%.

Tuesday 18:00 Marselisborg & Rosenborg

Design of different food materials based on the gelling ability of rice flour

Ana Morais¹, Patricia Fradinho², Isabel Sousa³, and <u>Anabela Raymundo⁴</u>

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Considering circular economy concept, the valorisation of by-products from the food industry, to obtain added-value foods, plays an important role. The main goal of this work is the development of food gelled with different applications in the food industry (toppings, puddings and baby foods), based on rice flour from broken grains. Portugal, the top country on rice consumption in Europe - 16 kg per capita, produces a specific type of Japonica variety - "carolino" rice - that is a traditional variety with differentiated starch properties to the development of gluten-free foods, namely gels. Rice milling creates about 40% of by-products, mainly forwarded to feed, which can still be of value to human food, making the product life cycle more efficient. In the present work, a detailed characterization of the gelling capacity of flour obtained from broken rice was performed, using SAOS tests: temperature (heating/cooling) cycles, time and frequency sweep tests, were set up inside the viscoelastic region. The texture properties of the gels (texture profile analysis) was also performed. It was found that 5% is the minimum concentration of rice flour which accounts for gel formation. In addition, flour concentrations above 8% have poorly acceptable sensory characteristics for any of the intended applications. The effect of sugar concentration on gel behaviour was also evaluated and 4% (w/w) sugar was the content with the best performance. The impact of sucrose substitution by sweeteners (xylitol and stevia) was also studied, and a significant impact on the gel rheology behaviour was not found. Texture and rheology characterisation of commercial toppings, puddings and baby foods were performed to use the results as a target for further develop the rice gels. To achieve this goal, the addition of hydrocolloids was tested: 0.25% of xanthan gum turned possible to obtain a typical topping gel structure; 1% of gelatine a pudding like structure and 0.25% of k-carrageenan a baby food like structure can be produced.

Tuesday 18:00 Marselisborg & Rosenborg

Efficacy of a new on-line rheometer to evaluate the rheological properties of gum tragacanth dispersions: effect of powder particle size and ultrasonication.

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The RheoStream(tm) technology (Fluidan) has been developed in order to satisfy the demand of automated and real-time techniques allowing for easier and more reliable data interpretation and utilization, by allowing the control and monitor of the complex rheological properties, especially viscoelastic properties, in a production process in real-time. The technology is based on a specially designed channel, optimized to differentiate a desired rheological property, where the pressure drop measurements obtained give information about the flow properties of the fluid. Our aim is to evaluate this new online technology with an off-line traditional rheometer, by using gum tragacanth dispersion as a simple model system. Gum tragacanth offers flexibility to change different variables. The variables chosen to fulfil this aim were gum concentration, and particle size reduction by physical grinding before dispersion preparation, and ultrasound treatment of the prepared dispersions. Efficacy of this new technology to measure steady and unsteady shear rheological properties for samples with different consistency and wide range of particle size were successfully assessed. It was found a good correlation between the results from the off-line and on-line rheometers. Best results were obtained with dispersion samples that were prepared by gum tragacanth powder with particle size less than 53um.

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Tuesday 18:00 Marselisborg & Rosenborg

Viscosity of a selection of edible oils and blends of some oils at different temperatures

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The viscosity of edible oils is a parameter used to describe quality. Liquid viscosity is also important regarding design of process equipment for the edible fat and oil industry. Rheological data are required for process piping design, pressure drop determination and in design of heat transfer equipment. Rheological properties are also of interest when modifying fats and oils, either the method used is fractionation, chemical, hydrogenation, enzymatic, blending or combinations of the mentioned methods. Blending can as an example be used in industrial applications to provide oils with improved composition related to stability, nutrition and functionality endowed with the characteristics requested by consumer preferences. Another aspect is related to authenticity of edible oils and fats, and methods available to detect or verify food authenticity. This is of course important both from a nutritional- and economical point of view since fats and oils have a big contribution in our diet as cooking or frying oils, salad oils or in food products formulations. The viscosity of a selection of oils and their blends, were measured in an MCR301 rheometer between 4 °C and 20 °C at varying shear rates. The results show the expected general temperature effect that the viscosity generally decrease with increase in temperature. There are also relatively large differences in viscosity between the different oils, especially at the lower shear rates tested.

Tuesday 18:00 Marselisborg & Rosenborg

Novel method for on-line rheology measurement in manufacturing of non-Newtonian liquids <u>Fridolin Okkels</u>

Fluidan, Copenhagen, Denmark

Companies who make or handle non-Newtonian liquids are challenged with finding a suitable process control method that can inform the process operators and control system about the current rheological properties of the liquids being processed. A range of high quality in-line viscometers are available, but no commercial instruments are able to monitor complex rheology, like viscoelasticity in real time. We introduce a novel measurement principle that allow for automatic, continuous near-real-time monitoring of e.g. viscoelasticity. The method is based on the detection of a specific pressure drop when the liquid flows through a complexly shaped channel. This pressure drop can be related to the complex rheology of the liquid. The method, currently being prototyped, has been applied for measuring viscoelasticity in a range of different liquids, such as food stabilizers, liquid detergents and Boger fluids, and we discuss the potential application in an industrial context.

Tuesday 18:00 Marselisborg & Rosenborg

Fluidisation of molten chocolate under vibration

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The fluidising effect of vibrations on tempered chocolate is widely utilised in industrial applications, e.g. to distribute chocolate in moulds. However, the detailed mechanics of fluidisation are not well understood. We study this problem by investigating the axisymmetric spreading due to vertical vibrations of a sessile drop of molten chocolate on a pre-existing layer of the same fluid. We performed experiments in which we subjected 5 ml drops to vibrations with a range of amplitudes and frequencies. The experiments show that the drop remains static under gravity and spreading only occurs when the acceleration of the substrate exceeds approximately 2 g. This onset of spreading is followed by a well-defined reduction in spreading time scales with increasing acceleration. Informed by rheological measurements, we model the molten chocolate as a generalised Newtonian fluid with a yield stress. Numerical simulations, based on the axisymmetric free-surface Navier-Stokes equations, capture the overall spreading dynamics observed in the experiments well but predict an earlier onset of spreading. The simulations enable us to investigate a single vibration cycle in order to understand the fluidisation mechanics. During the upward motion of the substrate the acceleration is enhanced relative to gravity. When it exceeds a critical value a large part of the drop fluidises almost instantaneously, which results in spreading. For the rest of the cycle, the acceleration is below the critical value and the drop remains static.

Tuesday 18:00 Marselisborg & Rosenborg

Spectroscopic tunable laser rheogoniometer for Weissenberg effect observation in condensed milk products as liquids with nonnewtonian viscosity

<u>Theodor Orehov</u>¹ and O. Gradov²

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This poster describes the setups for the Weissenberg effect observation in condensed liquids with non-Newtonian viscosity using tunable diode lasers, multispectral \ spectrozonal slow motion and time-lapse camcorders (for registration of kinetics and dynamics on different timescales), special metrological redundancy multi-axis spectroscopic techniques including streak camera, rotational five-axis robotized system [1]. This technique is based on our early papers [2] but is qualitatively different from the first implementations with photometric, refractometric and interferentional analytical techniques. To date the setups developed allow to perform spectrozonal mapping, automatic pattern recognition, one-to-one correspondence of the Weissenberg patterns in the reactive medium with a non-newtonian viscosity and the spectral parameters of the reacting medium with temporal resolution. The possibility of multispectral analysis achieved by using of a tunable laser diode provides a direct application of a selective chemometric approach to the "spectrorheology" of the analytes different in the absorption, reflection or emission parameters. The use of multi-axis system for the detector positioning at various angles not onli in

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plane, but also in Eulerian coordinates makes it possible to perform laser-based optical spectroscopy considering the optical patterns in the analyte. [1] A.V. Notchenko and O.V. Gradov Visualization, Image Processing and Computation in Biomedicine, Vol. 2, DOI: 10.1615/VisualizImageProc ComputatBiomed.2013005967 (2013) [2] Gradov O.V. Laser rheogoniometer for Weissenberg effect observation in condensed milk products as simple liquids with nonnewtonian viscosity. Dairy Farming Journal (ISSN: 2225-4269), 2(10), pp. 36-56 (2013) [in Russian].

Tuesday 18:00 Marselisborg & Rosenborg

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Mechanical properties of 67NR tumours are broadly independent of the immune status of the host mouse <u>Catherine T. Nordgård</u>¹, Shalini v. Rao², Morten J. Dille³, Tonje S. Steigedal⁴, and Kurt I. Draget⁵ ¹Department of Biotechnology, Norwegian University of Science and Technology NTNU, Trondheim, Norway; ²Department

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Tumour stiffness is increasingly seen as a clinically relevant parameter, with increased stiffness being linked to poorer prognosis (1), but it is also one that is not inherently easy to measure either in vivo or ex vivo. We have established a testing protocol for fresh ex vivo tumour tissue from tumour bearing mice using a Stable Micro Systems texture analyser fitted with a 2mm diameter cylindrical probe. The results of mechanical testing of 67NR tumours established in either in immune competent (Balb-c) or immune compromised (nude) mice are presented. The mean density of the tumours was similar in both groups (mean \pm S.D., Balb-c 0.00301 \pm 0.00108 gmm-3, Nude 0.00260 \pm 0.00141 gmm-3, n=10 in both groups). The force distance curves showed greater variability in the Nude mouse group compared to the Balb-c mouse group. Mean force at 5% strain \pm S.D. for the Balb-c and Nude mouse groups were 0.0016 \pm 0.0004g and 0.0019 \pm 0.0008g respectively. There were no statistically significant differences between the two groups. The data suggest that, in this tumour model, the presence or absence of T-cells does not significantly alter tumour stiffness. However, there may be more substantial differences if a more immunogenic tumour model was employed. (1)Macroscopic Stiffness of Breast Tumors Predicts Metastasis, Fenner et al, Scientific Reports 4, (2014)

Tuesday 18:00 Marselisborg & Rosenborg

Oscillatory Shearing Behavior of Rocket Leaves Powder Incorporated Dough

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Dough blended with rocket leave powder was subjected to small and large amplitude oscillatory shear. Small amplitude oscillatory shear data was fitted to a discrete relaxation model of elastic solids and to a critical gel model. The small amplitude relaxation spectrum was thereafter used to calculate the LAOS predictions of various large deformation models. The LAOS theoretical calculations using the Phan-Thien model showed good agreement with the first harmonic stress data, and only qualitative agreement with the third and the fifth harmonic stress values. Lissajous curves showed dissimilarity in shape between the experimental data and Phan-Thien model. The Network model of Sim et al. did not have the butterfly shape displayed in the Phan-Thien model, but it provided a worse fit to stress harmonics than the Phan-Thien model. An improved damage function was proposed, where time effect on network damage was taken into consideration, and fits to stress harmonics and to Lissajous stress-strain curves were significantly improved.

Tuesday 18:00 Marselisborg & Rosenborg

Surface rheological analysis of vegetable protein with pendant drop method

<u>Noemi Baldino</u>¹, Olga Mileti², Francesca R. Lupi³, Domenico Gabriele⁴, and Bruno de Cindio⁵ ¹DIMES, University of Calabria, Rende, Cs 87036, Italy; ²University of Calabria, Arcavacata di Rende, Italy; ³DIMES, University of Calabria, Rende, Cs 87036, Italy; ⁴DIMES, University of Calabria, Rende, Cs 87036, Italy; ⁵DIMES, University of Calabria, Rende, Cs 87036, Italy

Proteins are widely used to form and to stabilize the interfacial layers in multiphase systems, thanks to their surface activity and their ability to form highly elastic interfacial layers with gel-like behavior. Few studies are present in the literature about interfacial properties of proteins from vegetable seeds. Vegetable proteins could be good replacers of proteins from animal sources, in food products addressed to vegan/vegetarian consumers, and they could contribute to replace the gluten network in gluten-free food. In this study, the surface rheological properties of proteins from soy and hemp have been investigated. Proteins were used alone or in mixture with Transglutaminase, an enzyme able to cross-link proteins, modifying the rheological properties of their networks. The surface properties have been evaluated in dilatational kinematic with a pendant drop tensiometer at air/water (A/W) interface; static measurement, stress relaxation test and oscillations in linear conditions were used. The oscillating and relaxation tests have been performed at critical micellar concentration, previously evaluated by adsorption isotherms. The results evidenced a good surface activity for both proteins, a good viscoelastic behavior, a solid-like surface film and a time-dependence of the surface relaxation modulus. Furthermore, the results indicate that transglutaminase is not able to create cross-links in soy sample, but it is an effective tool to improve hemp surface properties, in both static and dynamic measurements.

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Tuesday 18:00 Marselisborg & Rosenborg

The rheology of food hydrogels based on the marine polysaccharide/gelatin polyelectrolyte complexes

Svetlana R. Derkach, Nikolay G. Voron'ko, Lyudmila K. Kuranova, and Nina I. Sokolan

Murmansk State Technical University, Murmansk, Russia

Polysaccharides are among the polymers that make up the fundamental components of life and constitute a major proportion of the Earth's biomass. Polyelectrolyte complexes (PEC) of polysaccharides with gelatin are currently considered as the most perspective stabilizers of dispersed systems in particular in food industry. The rheological properties of hydrogels based on PEC of gelatin with marine polysaccharides such as ?-carrageenan and chitosan have been studied. The rheological characteristics were measured in the mode of shear deformation on a rheometer Physica MCR302 using the cone-plate measuring cell. The interaction of gelatin and polysaccharides accompanied by the stoichiometric polyelectrolyte complexes formation in the aqueous phase has been studied by the methods of capillary viscometry, dispersion of light scattering, UV, FTIR and 1H NMR spectroscopy. The studied gels reveal linearity of the mechanical properties until amplitude of strain ? of about 10 - 30 %. Thus, it is believed that these gels at low strains (in linear viscoelastic region) show solid state behavior. For all concentrations of polysaccharides the storage modulus is much higher values of loss modulus. Increasing the concentration of chitosan (and hence chitosan/gelatin w/w ratios) causes increase in both G', and G'' in the entire considered frequency range. The observed impact of polysaccharides additions on the gels rheological properties is explained by formation of polysaccharide-gelatin PEC appears due to electrostatic interactions between opposite charged groups in biopolymers, hydrogen bonds and hydrophobic interactions also. The stoichiometric polysaccharide-gelatin complexes can be considered as new structure formers which show viscoelastic behavior in the linear range. The work was supported by the Russian Science Foundation (project N 16-16-00076).

Tuesday 18:00 Marselisborg & Rosenborg

Rheological approach to the development of a reference fluid mimicking crude oil behavior Galina Rodionova¹, Johan Sjöblom¹, and <u>Svetlana R. Derkach²</u>

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Crude oil itself is a toxic, volatile product that requires safe transportation and special routines in laboratory conditions. A reference fluid, also referred to as model oil, can be prepared to mimic crude oil and emulsion properties at various conditions. For industrial applications, mimicking flow properties of the crude oil and formation/separation of emulsions are of primary importance. In this study, a research effort was undertaken to develop a reference fluid modeling separation profile of W/O (water-in-oil) emulsions, rheological properties and pipeline flow behavior. As for emulsion preparation, different surfactant amounts, polymer mixtures and aqueous volume fractions were investigated to determine viscosity, stability and emulsion type. The droplet size distribution profiles of emulsions prepared in batches were estimated using a nuclear magnetic resonance spectroscopy, while in the pipeline droplet size distribution profiles were registered in-situ by a focused beam reflectance measurement probe. Rheological properties of the heavy crude oils with large presence of asphaltenes are highly sensitive to the interactions between its components under applied shear rates and temperatures. The W/O emulsion rheology may vary between the crude oil and reference fluid. Presence of the emulsions for both fluids. Viscosity measurements at a wide range shear rates, droplet size distributions and separation profiles of the emulsions were used as tools for predicting if the reference fluid and crude oil will have similarities in the flow properties when subjected to actual pipeline conditions. The work was financially supported by the Russian Foundation of Basic Research (project N 16-58-20008). The authors acknowledge the partial financial support from The Multiphase Flow Assurance Innovation Centre (FACE) and Russia and the High North/Arctic (NORRUS) programme.

Tuesday 18:00 Marselisborg & Rosenborg

Developing cultured meat scaffolds of extruded vegetable-based proteins

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Global meat consumption per capita doubled between 1961 and 2009. Consequently, we are eating more meat than is sustainable for our environment and health, and face major challenges for meat production in the future. One is to be able to meet the increasing demand, in particular in rapidly developing countries. Another is to make meat production environmentally sustainable. In this project, we investigate a new approach to produce cultured meat by growing skeletal muscle cells on fibrous scaffolds made from vegetable-based protein. Hemp, maize and pea protein fibers were extruded using a Goettfert Rheograph 2000 capillary rheometer. Water was used as plasticizer, and following composition optimization trials, maize and pea were processed with a moisture content of 50% and hemp 40%. A circular die with an aspect ratio of 5/0.5 (0.5 mm die diameter, 5 mm die length) was used, The extrusion apparent shear rate was maintained at 9200 1/s and the temperature at 80C on all heating elements. The extruded fibers were sterilized either in ethanol or with UV-ozone and incubated with C2C12 skeletal muscle cells for one week in DMEM cell culture media supplemented with glucose, 1% Pen Strep and 10% FBS. Cells were fixed and stained to visualize the cell nucleus (Dapi) and the actin cytoskeletal filaments (rhodamin phalloidin), and imaged by confocal microscopy. Hemp protein fibers dissolved slightly in culture medium and were infected with bacteria. No muscle cells grew in hemp cultures. Fibers of maize and pea remained intact after the incubation period and supported muscle cell attachment and growth, although there were still bacteria in the pea fibre samples after ethanol sterilization. It was shown that the muscle cells grew best on maize protein fibers, and began to align in preparation for myotube formation. Maize protein is a promising scaffold for skeletal muscle cell growth. Longer culture times should be investigated to see if mature muscle fiber formation is possible to achieve in these constructs.

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Tuesday 18:00 Marselisborg & Rosenborg

Shear-induced textures in calf-thymus DNA solutions

Lourdes Monica M. Bravo Anaya¹, Denis C D Roux², Frédéric Pignon², Marguerite Rinaudo³, Armando Soltero¹, and Gabriel Landazuri¹

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DNA solutions dynamics, as well as their flow properties, are important for the understanding of DNA functions and cell division. Moreover, DNA is considered as a model system for the study of molecular dynamics of semi-rigid charged polymers. In this work, the evidence of DNA shear-induced textures is explored as a function of DNA concentration $(2.0 \le C_{DNA} \le 40.0 \text{ mg/mL})$ and ionic concentration. To reach a better understanding of the molecular organization of DNA solutions, mechanical and flow birefringence measurements in combination with different visual observations were used in this work. Firstly, the conditions under which appears a stress plateau in the flow experiments were identified as a function of DNA concentration and the imposed shear rate. Then, birefringence measurements and visualizations revealed the appearance of shear-induced textures leading to the organization of flow-oriented DNA subdomains, which takes place when the flow curve exhibits a shear stress plateau. The role of electrostatic interactions in the appearance of the shear-induced textures was then discussed in terms of the ionic concentration influence on DNA flow behavior. Liquid crystalline phases, with textures similar to those of liquid-crystalline hexagonal phases, were then observed under static conditions by cross-polarizer-analyzer microscopy for concentrated DNA solutions with concentrations higher than 40.0 mg/mL, which resemble to the textures obtained under flow.

Tuesday 18:00 Marselisborg & Rosenborg

Rheological properties of kuzu starch pastes in the mixture with galactomannans

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Kuzu (kudzu) is an edible plant from Southeast Asia. For centuries, it has been known for its unique properties: is effective in a fight against addictions, does not contain gluten or lactose, helps in weight loss and body detoxification, has a beneficial effect on cardiovascular system, and prevents cancer. Starch contained in the kuzu root provides an alternative to thickeners and binders such as gelatin or potato starch. In the literature, there is lack of comprehensive information about the structure and viscoelastic properties of kuzu starch pastes in the mixture with widely available thickening/gelling agents - galactomannans.

The aim of this study was a comprehensive characterization of rheological properties of 3% (w/v) Japanese kuzu starch pastes in the mixture with 0.3% (w/v) galactomannans extracted from seeds of leguminous plants: fenugreek gum, guar gum, tara gum, and locust bean gum (carob). The suspensions were pasted at 95°C for 75 minutes and subjected to oscillatory and creep tests. The obtained results in the form of storage modulus $G'(\omega)$, loss modulus $G''(\omega)$ and shear creep compliance J(t) were described by means of the new modified fractional Kelvin-Voigt model created on the basis of differential calculus of fractional order, and Fourier transform. This model fully characterized dissipative processes in the entire range of viscoelastic plateau. It allowed to determine several material constants comprehensively describing structure and viscoelastic properties of kuzu pastes, depending on mannose-to-galactose ratio in galactomannan molecule. It is particularly important in materials engineering, in product design processes concerning biopolymers. Conducted basic research may provide a starting point for applied research in food and pharmaceutical industries. Perspectives of their application in economic practice may concern mainly people suffering from: celiac disease, lactose intolerance and alcohol or nicotine addiction.

Tuesday 18:00 Marselisborg & Rosenborg

A versatile subphase exchange cell for interfacial shear rheology

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Interfacial rheological properties play a key role in the stability of a wide range of high-interface materials and thin films. For many systems, it is desirable to understand the response of the interface to a change of composition in the surrounding bulk phases. Stimuli, such as changes in pH or electrolyte concentration, can have a major effect on the structure and properties of the interfacial layer, or induce adsorption and desorption phenomena. Shear rheology is a particularly sensitive measure of such changes, as it only probes the extra stresses in the interface, regardless of possible variations in interfacial tension. In the present work, a widely used geometry for interfacial rheometry, the double-wall ring, is modified to enable subphase exchanges. The trade-off between the speed of exchange and the stress exerted by the flow in the subphase onto the interface is carefully considered. The optimal geometrical design is found by employing Computational Fluid Dynamics (CFD). A geometry with inlets positioned at the bottom and outlets near the interface minimizes the mixing time. Experiments on interfaces with colloidal particles and proteins, subjected to changes in electrolyte concentration and pH, respectively, are used to evaluate the performance of the setup.

Tuesday 18:00 Marselisborg & Rosenborg

Flow Curves of Biopolymer of Chia (Salvia hispanica L.) with Monovalnets Ions Emmanuel Flores Huicochea¹ and Rodolfo Rendon Villalobos²

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The flow curve, viscosity vs strain rate, of chia (Salvia hispanica L.) biopolymer on the concentration interval from 0.037 to 0.97 %, at two temperatures (25 and 40 °C) and ions Na+ (0,10, 25 mM) are reported. The flow curves of biopolymer of chia a two temperatures and ions

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showed that the raise on strain rate produce a reduction on viscosity similar to others biopolymers. The maximal viscosity were on the interval 0.1 a 20 Pa.s on the concentration interval 0.1 a 20 Pa.s, at 25 °C, the increase on ions produce a decrease on maximal viscosity. However, the temperature increase from 25 to 40 °C, over the concentration interval from 0.1 a 1%, produced an increase on maximal viscosity (300 Pa.s), at the same temperature (40 °C), but with ions (25 mM Na+) there is a reduction in viscosity. The effect of temperature was increase the maximal viscosity and the increase on ions decrease the viscosity. The temperature and ions has effect over molecular volume, the first increase and the second decrease, due chia biopolymer is a polyelectrolytic.

Tuesday 18:00 Marselisborg & Rosenborg

Rheology of aqueous Laponite-scleroglucan mixed systems

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Both Laponite and scleroglucan can find several applications in various fields (from industrial to biomedical one) in virtue of their peculiar features and rheological properties displayed in aqueous phases. Structural states of Laponite dispersions strongly depend on concentration and ionic strength. When attractive and repulsive interparticle interactions are so effective that they lead to arrested states (attractive gel or repulsive glass), the rheological behavior of the dispersion undergoes a sharp transition, from quasi-Newtonian to markedly shear thinning and viscoelastic. Conversely, scleroglucan solutions gradually change to weak gels with increasing polymer concentration. The present work deals with aqueous Laponite-scleroglucan mixed systems, obtained according to different preparation modes and examined at different aging times, and is aimed at examining how much the content and proportion of both components affect the viscoelastic and flow properties of the mixed system.

Tuesday 18:00 Marselisborg & Rosenborg

An alternative elongational method to study the effect of saliva on dysphagia-designed fluids

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Dysphagia is a highly prevalent clinical condition related to any dysfunction that impairs optimal and safe delivery of food and drinks during swallowing. Thickened fluids for dysphagia management (TF) are in general non-Newtonian hydrocolloids dispersions. It is now assumed that extensional rheology may also play an important role in the development of dysphagia-designed products, since thickened fluids may undergo elongational deformations during oral processing. Capillary breakup extensional rheology (CaBER) measurements of such fluids seem promising, but are limited by the formation of apparent non-cylindrical and poorly reproducible filaments during uniaxial elongation. In this work, axial force measurement is suggested as an alternative for monitoring the elongational behaviour of such fluids. To our knowledge the measurement of axial forces developed in dysphagia-designed fluids during uniaxial elongation is addressed for the first time. TF were studied by means of a capillary break-up extensional rheometer (CaBER) with an attached high-speed camera (Photron Fastcam Mini UX100) and a force sensor (Kistler 9215A). TF prepared with commercially available powder thickeners were tested, both pure and mixed with reconstituted salivary a-amylase (SAA). The results obtained provide a first view of the impact of SAA on the elongational properties of fluids containing different types of thickeners, differentiating between gum-based (GB) and starch-based (SB), when considering the filament evolution and the axial force seconded during elongation. A differentiation between homogenous and non-homogenous formulations was also possible Monitoring axial forces during capillary break-up process was found to be a quick alternative method to identify structural changes influencing the elongational properties of highly concentrated dysphagia-designed fluids in the presence of SAA, for which the conventional CaBER experiments are technically limited.

Tuesday 18:00 Marselisborg & Rosenborg

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In-line Rheological Quantification and Microstructural Characterization of Novel High Protein Vegetable Foods obtained through Extrusion Cooking

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Novel high protein vegetable blends containing potato protein, oat protein and wheat bran were extruded in a single screw laboratory extruder using potato starch (PS) and potato fibers (PF) as structuring agents. In-line rheological measurements were performed with slit die to characterize dough shear viscosities (η_a) as function of shear rates, wet moisture contents (MC_w) and feed compositions. The blends exhibited shear thinning behavior and their consistency (*K*) and flow behavior index (*n*) were determined from power law model. In general, as MC_w increased, *K* decreased while *n* departed towards Newtonian behavior. Bhattacharya and Hanna (1986) model was employed to study η_a as function of both shear rates and MC_w simultaneously. The model indicated that MC_w exerted a strong influence on η_a for all compositions investigated. Flow images and microstructural investigations from screw freezing experiments suggested dispersed plug flow during extrusion cooking. Segregative phases of proteins, PS and PF in functional zones due to biopolymer incompatibility led to continuous and dispersed phases according to principles of `Suspension model'. Size and shape distribution of proteins and PF in the extrudates were evaluated from bright field and polarized light microscopic images. Image analysis revealed that mean equivalent diameter of proteins did not alter considerably with feed compositions while roundness of proteins were affected by feed compositions and was lowest for the blend containing PF only.

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Tuesday 18:00 Marselisborg & Rosenborg

"Hybrid hydrogels by the co-assembly of chitosan with phospholipids"

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Chitosan's (Ch) and Phospholipids (P) have been considered attractive biomolecules, due its set of remarkable biological properties and have been used as building blocks to fabricate functional nano-bio structures (e.g. nanoparticles, capsules/liposomes, emulsions and organogels). At this study we have developed hybrid hydrogels by the co-assembly of chitosan with phospholipid self-assembled particles [1]. The effect of phospholipid content on the morphological and physic-chemical properties of the Ch/P hydrogels was evaluated by Scanning Electron Microscopy (SEM), Dynamic Light Scatering (DLS), Rheology and swelling index measurements. It was observed that the lower concentration of phospholipid content. Morphologically, the internal structures of Ch/P hybrid hydrogels was found to contain nanopores that facilitates the penetration of water and swelling, which tend to slightly increase with the increase of phospholipid content. The use of biocompatible materials, such as chitosan and phospholipids, to produce Ch/P hybrid hydrogels in mild conditions, suggest their potential to be used within life sciences applications. References: [1] Mendes AC, Shekarforoush E, Engwer C, Beeren S, Gorzelanny C, Goycoolea FM., Chronakis IS, (2016), Co-assembly of chitosan and phospholipids into hybrid hydrogels, Pure and Applied Chemistry, In press.

Tuesday 18:00 Marselisborg & Rosenborg

Relaxations in Neat Amorphous Drugs and its Implication on Physical Stability

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Molecular mobility (relaxation) refers to inter or intra-molecular motion and can be generally classified into the primary (α) relaxations and secondary (β) relaxation. It is generally agreed that relaxations are responsible for the physical stability of amorphous drugs. Physical stability refers to the ordering of molecules (onset of recrystallization) in a disordered molecular system. The objectives of this study were, to characterize molecular mobility in five neat amorphous drugs, to correlate their relaxations to their observed long term physical stability (298 K, 0% RH) and, to determine the physical stability of the drugs when stored below their β -relaxation temperature, i.e. at 193 K. Amorphous drugs were characterized with solid state techniques including X-ray powder diffraction (XRPD) and differential scanning calorimetry (DSC). Relaxations were studied via dynamic mechanical analysis (DMA). From the tan d DMA signal, we identified the α -relaxation peak (glass transition temperature, T_{g,DMA}) and the β -relaxation peak (T_{β}) which is an indication of molecular mobility at sub ambient temperatures. When the T_{g,DMA} and T_{β} were correlated to their physical stability, we found a good correlation between T_{β} rather than the T_{g,DMA} and the physical stability of the drugs. When the drugs were stored below their T_{β}, i.e. 193 K, they remained physically stable for the investigated period of 102 days. This relaxation study in amorphous drugs has shown that β -relaxation maybe the main relaxation phenomenon which determines how physically stable the neat amorphous drugs is amorphous drugs is also below the relaxation maybe the main relaxation phenomenon which determines how physically stable the neat amorphous drugs is also below the relaxation maybe the main relaxation phenomenon which determines how physically stable the neat amorphous drugs is also below the relaxation maybe the main relaxation phenomenon which determines how physically stable the neat amorphous drug is.

Tuesday 18:00 Marselisborg & Rosenborg

Rheological characterisation of skim milk concentrates with different dry matter contents

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The production and properties of skim milk concentrates have recently been receiving increasing interest. Skim milk concentrates can be produced in several different ways, all with the main aim of increasing the dry matter content of the skim milk by removal of water. Such concentrates might then be used directly in a spray drying process for production of powdered products, but could also be sold and/or transported as concentrates, provided an adequate stability can be obtained. During and after the concentration process, the properties of the milk will change. When water is removed from milk the spacing between the emulsified and dispersed particles will change, and this can result in new or more interactions. The rheological properties, primarily the viscosity, of a concentrate is of major importance for the handling and possible further processing, since both pumping and atomization behaviour are highly dependent on the viscosity. Furthermore, when concentrates are stored at relatively high temperature, e.g. as buffer prior to spray drying, the viscosity could increase significantly over time. The aim of the present study was to characterise the rheological properties of skim milk concentrates with different dry matter contents ranging from 20% to 50 % total solids (TS). The concentrates were produced by reconstitution of skim milk powder in water to avoid variation from milk samples. The measurements included flow curves describing the apparent viscosity at a broad range of shear rates (0.1-1000 s⁻¹) as well as oscillatory measurements of changes occurring during storage at high temperature. The flow behaviour of skim milk and concentrates with low TS concentration is very close to being Newtonian, but as the TS concentration increases, a change towards shear-thinning behaviour is observed. Results will be presented showing the changes occurring in rheological properties of skim milk concentrates as functions of dry matter content, temperature and storage time.

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Tuesday 18:00 Marselisborg & Rosenborg

Development of bio-based superabsorbent polymeric matrices based on functionalized soy protein

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As an alternative to acrylic superabsorbent polymers (SAP), this work studies the feasibility of obtaining natural-based SAP materials via soy protein (SPI) functionalization using different amounts of ethylenediaminetetraacetic dianhydride (EDTAD) or succinic anhydride (SA) as acylating agents. After protein modification, blends containing 50 wt.% protein (unmodified SPI or acylated SPI) and 50 wt.% glycerol were mixing in a two-blade counter batch mixer. Temperature ramp DMA compression tests conducted on them point out the effect that a more hydrophilic protein character, as a consequence of the presence of a large amount of COO- groups, exerts on their rheological response. Thus, it was observed that the acylated blends require a maturation time of at least 24 h for getting higher elastic modulus in the low-intermediate testing temperature range (0-60 °C). On the other hand, the increase in tan d values for acylated SPI blends, over a broader temperature range, together with their higher sensibility to temperature, may be regarded as a favourable factor which facilitates their lab-scale injection molding. On the other hand, the acylated bioplastics samples processed by injection molding are less fragile than unmodified one, since the maximum strain before breaking rises. Regarding their water uptake capacity, bioplastic samples is strongly enhanced for those prepared from acylated SPI (with values of up to 3650 wt.%) compared to the moderate value obtained for the reference sample (160 wt.%). Thus, all acylated bioplastics comply the water uptake level required to be considered as SAP materials and could be re-used at least twice without losing their water uptake capacity. Interestingly, freeze-dried acylated samples (after 1 freeze-drying cycle) may be regarded as highly promising candidates for applications in which maintaining the dimensional stability during service is not crucial (e.g. in agriculture and horticulture).

Tuesday 18:00 Marselisborg & Rosenborg

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Rheological Characterization of Alternative Contrast Agent-containing Thickened Fluids for Dysphagia Assessment

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Diet modification (i.e. control of bolus flow properties) is part of several strategies for dysphagia management and is used to avoid aspiration pneumonia in dysphagic patients. Texture or consistency modification of liquids or solids is commonly done by using food thickeners in powder form. Many of them are starch-based, although new products are now available based on amylase resistant gums. Ideally, the most appropriate modification of food consistencies should follow from a clear assessment of the swallowing problem. Videofluoroscopic swallowing studies (VFSS) have become a kind of golden standard for the evaluation of swallowing and, thus, dysphagia. The standard contrast agent for videofluoroscopy studies is barium sulphate. The corresponding barium sulphate-based thickened fluids can be found as ready-to-use products in USA. However, they are very expensive and, in most cases, separate into phases during ageing. Another common practice in hospitals is to add barium sulphate to standard foods, without taking into account that this addition modifies the rheological properties of the food and, on the other hand, the final viscosity depends on the characteristics (i.e. particle size distribution) of the barium sulphate used. An alternative to the use of this "standard" contrast agent has been more recently suggested and is based on the thickening of an iodinated radiopaque contrast medium solution with a powder thickener (starch or gum based). This study deals with the rheological characterisation of thickened fluids for different dysphagia stages (nectar, honey and pudding-like) with a thickened iodinated radiopaque contrast medium solution and their matching with the rheological properties of the corresponding commercial contrast media containing barium sulphate.

Tuesday 18:00 Marselisborg & Rosenborg

Thixotropic properties of chitosan systems - the effect of shear deformation

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Chitosan is an amino polysaccharide, and as a biocompatible and biodegradable biopolymer, has been widely used in medical, food industries, cosmetics as well as in wastewater treatment. Chitosan systems in the form of hydrogels are subject of many studies in the literature concerning tissue engineering and drug delivery systems. The paper presents the study of chitosan colloidal system in acidic medium (pH⁻1) and with addition of neutralizing agent β -Glycerophosphate disodium (pH⁻7). The experimental measurements were carried out for chitosans of various backgrounds (crab, shrimp) and molecular weights. Measurements of the rheological properties were performed in order to determine the flow curves. The experimental data were collected in the range of shear rate from 10-1 to 103 s-1, and temperature from 20 to 40°C, both for ascending and descending shear rate. Additionally, three interval thixotropy test (3ITT) was performed to determine the effect of shear deformation on the sample. Taking into account experimental data, the cumulative curves of thixotropic energy were determined. Based on experimental data and DLVO theory an analysis of interchain interactions have been presented. It was stated that the presence of the positively charged amino groups in chitosan structure leads to the electrostatic repulsion. Shear deformation results in disentanglement of polymer chains. Higher temperature causes neutralization of amino groups. Thus, there is a loss of the electrostatic repulsion and domination of hydrophobic forces. This leads to the formation of intermolecular bonds between chitosan chains and in consequence to phase transition from sol to gel. Experimental data from 3ITT revealed dependency between molecular weight and

degree of deformation. The higher the molecular weight, the lower the value of degree of deformation. Acknowledgements Research was financed by National Science Centre, Poland - Grant NCN UMO-2014/15/B/ST8/02512

Tuesday 18:00 Marselisborg & Rosenborg

Structuring properties of citrus-based dietary fibres in aqueous systems

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Dietary fibres are carbohydrate polymers which are not hydrolysed by the endogenous enzymes in the small intestine of humans; their consumption is increasing, also according to the suggestions of the World Health Organisations, because it was observed that a significant intake of fibre helps in preventing coronary heart disease, stroke, hypertension, diabetes, obesity, and certain gastrointestinal diseases. From a technological point of view, it is commonly recognized that, soluble and non-soluble dietary fibres have effects on the rheological characteristics of water phases: they are characterised by gelling ability and hydration properties, and the fibre-supplemented foods show viscoelastic behaviour influenced by the addition of fibres. An investigation on the effect of fibers on the rheological properties of the solvent into which they are added can be useful to tune the rheological properties of food systems like emulsions, beverages, sauces, etc. In this work, the effects of dietary fibre obtained from citrus fruits, were investigated in simple systems based on fibre dispersed in water at different concentration. Steady and dynamic tests were used to determine viscosity and dynamic moduli of dispersions at increasing fibre content aiming at determining the potential thickening and/or gelling properties of this material and a potential threshold concentration corresponding to the limit to have a gel formation. It was observed that depending on the adopted conditions this fibre can be used either to modify viscosity (thickening agent) or to build a structured gel.

Tuesday 18:00 Marselisborg & Rosenborg

Macro- and micro- rheological characterization of human bronchial mucus

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The mucociliary function of the bronchial epithelium ensures the continuous clearance of the respiratory system. Any dysfunction might lead to infections and inflammations and eventually cause death of the patient. Therefore, the understanding of the mechanisms behind this function is a major issue in the field of respiratory disease. The mucociliary clearance relies on two main elements: mucus and cilia beating coordination. Our objective in this study is to measure the mucus rheology, and in particular, to consider the mucus viscoelastic properties as a potential marker for the diagnosis of respiratory disease (COPD Chronic Obstructive Pulmonary Disease ...). Studies on mucus rheology have already been performed, but essentially on sputum, or reconstituted mucus. We performed rheological experiments on mucus extracted from ALI (Air Liquid Interface) cultures of bronchial epithelium reconstituted from a bronchial biopsy. Our approach consists in combining a standard macro-rheology to micro-rheology performed with optical tweezers in order to quantify the mucus viscoelastic properties and understand its behavior at different scales, from the cilia scale up to the length scale on which mucus is transported. Our results confirm the shear-thinning behavior and the elastic nature of the mucus. We show that mucus is fragile and that it ruptures when increasing the shear rate even for frequencies lower than the cilia beating frequency (~15 Hz). We compare macro and micro rheology and observe an elastic plateau at the macro-scale but a viscous behavior at the micro-scale. Using optical tweezers, we show that adhesion is involved and can explain the difference between the mechanical properties measured as a function of the probed length scale. This specific methodology allows us to compare samples corresponding to different patient pathologies and could be successfully applied to the hypersecretion of mucus from patients with Cystic Fibrosis.

Tuesday 18:00 Marselisborg & Rosenborg

Extrudate swell of linear polystyrenes

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This work aims to achieve a molecular understanding of extrudate swell (also called 'die swell'). We present predictions of extrudate swell using the tube-model-based Rolie-Poly constitutive equation combined with the Lagrangrian finite element solver flowSolve. We find a molecular weight independence of the swelling when the flow speed is scaled by the Rouse Weissenberg number. The roles that both chain orientation and stretch play in determining extrudate swell are clearly identifiable from plots of swelling ratio against Weissenberg number. We also present complementary experimental results performed isothermally inside a Multi-Pass Rheometer. The predictions for swelling ratios of monodisperse polystyrene closely match those from experiments up to Rouse Weissenberg numbers of ~7 above which swelling is over predicted by flowSolve. Simulations of a bidisperse melt are also presented where an increased chain stretch time for the longer component results in a better fit to experimental data than an uncorrected simulation.

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Tuesday 18:00 Marselisborg & Rosenborg

Effect of lift force on dense gas-fluidised beds of non-spherical particles

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Particle aggregates are frequently processed in industrial apparatus such as pneumatic conveyors, bed gasifiers and fluidised bed reactors. In numerical models of these processes, particles have traditionally been represented as spheres, thus limiting complexities associated with drag or lift forces. However, spherical particles are not representative of the entities encountered in real systems. For example, non-spherical biomass particles of varying aspect ratios are used in the production of biomass fuels. Thus far, there is limited literature in relation to hydrodynamic forces experienced by non-spherical particles under fluidised conditions. In fluidised beds, particles will experience varying lift force conditions dependent on the orientation of the particle relative to the direction of the fluid velocity.

In this study, we investigate numerically the effect of differing lift force coefficient correlations on spherocylindrical particles of varying aspect ratios. We employ correlations derived from previous simulations on non-spherical particles [1] and aerofoil dynamics [2] in simulations. Particle interactions are modelled using the Open Source engine CFDEM, which uses the OpenFOAM computational fluid dynamics (CFD) solver to describe the fluid component and LIGGGHTS to implement discrete element method (DEM) calculations [3]. We investigate the importance of lift forces on non-spherical particles under dense fluidised conditions and compare results to the case of spherical particles where lift forces are often neglected.

REFERENCES

[1] ZASTAWNY M., MALLOUPPAS G., ZHAO F., B. van WACHEM, (2012), "Derivation of drag and lift force and torque coefficients for non-spherical particles in flows", Int. J. Multiphase Flow, 101, 288-295.

[2] HOERNER, J., (1965), "Fluid-dynamics drag" Hoerner Fluid Dynamics.

[3] MAHAJAN, V. V., NJISSEN, T. M. J., FITZGERALD, B.W., HOFMAN, J., KUIPERS, H. AND PADDING, J. T., "Fluidisation of spherocylindrical particles", Powders & Grains 2017.

Tuesday 18:00 Marselisborg & Rosenborg

Practical mapping of the draw resonance instability

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In film casting and fiber spinning processes, molten material is extruded through a die and taken up by a rotating chill roll, with the socalled draw ratio, i.e., the ratio of the inlet to the take-up velocity. Exceeding a critical draw ratio leads to oscillations of flow velocity and film thickness and width or, respectively, fiber diameter, which is commonly known as draw resonance.

In this work, we present a mapping strategy which enables a quick and practical oriented analysis of the draw resonance behavior for film casting and fiber spinning. For this purpose, film casting and fiber spinning models including gravity and inertia as well as the effects of neck-in in film casting and surface tension in fiber spinning are examined by means of linear stability analysis. Besides Newtonian models, the simplified PTT model is applied to account for viscoelastic effects as well. Proper scaling of the system variables reveals dimensionless control parameters with strong correlation to practical application, e.g., the inlet velocity and the fluidity.

The stability maps visualize isolines of constant critical draw ratio in the parameter space. This enables, besides a comprehensive overview of the stability behavior, the identification of distinct dynamical regimes, within which one or several effects can be neglected, as for instance parameter regions of unconditional stability in the case of dominating inertia or unconditional instability in the case of dominating surface tension in fiber spinning.

Tuesday 18:00 Marselisborg & Rosenborg

Observation of jet buckling instabilities for various non-Newtonian fluids

Romain Castellani, Alexandre Antoniotti, Anselmo S. Pereira, and Rudy Valette PSL Research University, MINES ParisTech, CEMEF, Sophia Antipolis, France

Jet buckling instabilities are found in multiple industrial applications, such as dairy products containers filling or rocket boosters loading. The way the filling goes is critical as it will affect end-use properties. For high viscosity products or high filling rates, the jet of fluid will spread or form different types of coils depending on its velocity and diameter. Regarding the case of Newtonian fluids, the diameter of this coil, the winding frequency and the jet radius at impact are well known for a large range of flow rates and falling heights [1]. Multiple regimes were found, depending on the balance of gravity, inertial and viscous forces (and thus fluid characteristics as viscosity or density). However, a few questions arise:

Does a non-Newtonian fluid follow the same kind of physics (eventually re-scaled by a modified viscosity function)?

Once the fluid coil reaches a certain height, how does it collapse (entrapping gas bubbles)?

What happens on a tilted (slipping) plane?

In order to answer these questions, different materials were used, including transparent non-Newtonian fluids. Buckling is observed thanks to a high speed camera and coiling parameters (frequencies and diameters, as discussed before) are measured. The amount of air trapped during the filling is also addressed with regard to the collapse frequency of the coils and their internal volume. Comparisons between existing models on Newtonian fluids and our results are then discussed. In addition, direct observations on how the liquid "rope" forms the coil (local flexion or torsion at the impact point) are made using a few amounts of particles as markers in the various fluids.

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PO82

[1] Neil M. Ribe et al., Liquid Rope Coiling, Annual Review of Fluid Mechanics Vol. 44: 249-266 (2012)

Marselisborg & Rosenborg Tuesday 18:00

Establishing a traceability chain for the automation of viscosity measurements in the oil drilling industry **Ronald Pagel**

Chemical Physics and Explosion Protection, Physikalisch-Technische Bundesanstalt, Braunschweig 38116, Germany

Drilling automation is a key driver for improving safety and efficiency in the exploration of oil and gas fields. Drilling fluids have non-Newtonian flow behaviour to fulfil a variety of functions. Precise knowledge of the viscosity of the drilling fluids and its dependence on operational parameters is vital for the prediction of, among others, pump pressures and well clogging due to settling of particles. For this purpose and with view on cost efficiency, several in-/at-/on-line viscosity sensors in a flow loop on a rig have to be calibrated in place with shortest downtimes. This contribution focuses on the traceability chain and uncertainty of measurement of the rheological properties of drilling fluids. Key steps in the chain are based on the provision of non-Newtonian reference liquids (NNLs) with flow curves similar to the ones of drilling fluids in the ranges 0.5 1/s to 2500 1/s and 0 Pa to 200 Pa. Proposed NNLs are composed of block copolymers in hydrocarbon oils. The steps in the traceability chain are in particular: 1. Thorough calibration of a "primary" reference rheometer traceable to the Système international d'unités (SI); 2. Certification of the flow curve (viscosities in dependence on shear rates) of a reference NNL; 3. Calibration of a lab rheometer by using the NNL; 4. Production of a reference NNL with specified viscosities by a standardised method and subsequent determination of its flow curve by using the lab rheometer; 5. Calibration of the in-/at-/on-line viscosity sensors by circulating this liquid. The NNLs are established to provide comparable viscosity data and to ascertain that quantities are generally transferable between physical relations. Shear rate and temperature (including shear heating) have been identified as main contributors to the uncertainty budget. The main advantage of the proposed traceability chain lies in performing steps 3 to 5 on a rig, resulting in sensors calibrated in a desired viscosity range in one run with bigger volumes of a well-characterised low-cost NNL.

Tuesday 18:00 Marselisborg & Rosenborg

Rheology and DMA measurements on magnetorheological fluids

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Magnetorheological (MR) Fluids are suspensions of micron-sized particles of magnetizable materials. These suspensions are characterized by the tunability of their rheological properties by means of magnetic field application, a phenomenon known as the MR effect. The commercial trademark of MR Fluid used in the present work is MRHCCS4-A from Liquid Research Limited (UK). In addition, we used a non-commercial MR fluid characterized by having particle content close to the maximum-packing fraction. The magneto-rheological properties of were measured at several magnetic field intensities in shear and compression allowing a comprehensive characterization of their mechanical properties. The results show that when the magnetic field was varied, from 0 mT and 1000 mT the change in the storage compression modulus is more than 10 times bigger than the change in storage shear modulus for the commercial fluid fluid MRHCCS4-A reaching the saturation. The change in the storage compression modulus and the shear compression modulus iis pretty similar for the highly concentration supspesion (carbonyl iron powder in oil).

Marselisborg & Rosenborg Tuesday 18:00

Analyzing Solid and Molten Polymers with Rotational Rheometers

Jan P. Plog¹ and Fabian Meyer²

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Polymers are large molecules consisting of repetitive units of smaller molecules bonded together and forming long chains. They are used in a broad variety of applications and are ubiquitous in our everyday life. In solution for example, polymers can be used as thickeners or stabilizers in food and personal care products. In solid state they are used for casings, packaging or composite materials. For these types of applications polymers are processed at elevated temperatures in a molten state. Due to their chemical structure and high molecular weight, polymers exhibit a complex flow and deformation behavior. They are so called viscoelastic materials, showing both, viscous and elastic properties. Which behavior is dominating depends on the molecular structure itself, as well as the testing or processing conditions. Too much elasticity can lead to flow anomalies and unwanted effects during many common processing steps. One well-known example is the swelling of a melt stream when exiting the narrow die of an extruder.

Knowing the viscoelastic properties of a polymeric material is therefore essential to optimize formulations and blends as well as to adapt a process to the properties of a given material. Rheology has proven to be an excellent tool to analyze the mechanical properties of polymers in their different states. Various testing methods are available for a full rheological characterization of polymeric materials. The intention of this poster is to provide an overview of the information gained from rheological tests performed with solid and molten polymers and to show up its significance for optimizing processing steps as well as final product performance.

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Tuesday 18:00 Marselisborg & Rosenborg Viscosity Measurements with a Small Scale Conical Twin Screw Extruder

Jan P. Plog¹ and Fabian Meyer²

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The Thermo Scientific HAAKE MiniLab 3 is a small scale conical twin screw extruder that enables the compounding and processing of sample quantities down to about 7 ml. It is equipped with a back flow channel and a bypass valve, which allows for controlling the residence time of the sample inside the compounder. The patented design of the back flow channel consists of a slit capillary with two pressure transducers that are used to measure the pressure drop inside the flow channel. When a sample is passing through the flow channel the resulting pressure drop can be used to calculate an apparent shear stress. From the selected screw speed and the measured back pressure an apparent shear rate can be obtained. The shear stress and the shear rate values can be used to calculate the relative sample viscosity at different screw speeds. This principle enables to determine the shear thinning behavior of polymer melts with a small scale bench top extruder. In this contribution we present viscosity data of different LDPE blends measured with the HAAKE MiniLab 3. The results are compared with complex viscosity data obtained from oscillatory measurements with a rotational rheometer.

Tuesday 18:00 Marselisborg & Rosenborg Optimized Test Parameters to Monitor Gelling and Phase Transitions Jan P. Plog¹ and Klaus Oldörp²

¹Material Characterization, Thermo Fisher Scientific, Karlsruhe, Germany; ²Material Characterization, Thermo Fisher Scientific, Karlsruhe, Germany

Whenever the rheological properties of a substance change drastically, it can be quite challenging to design a rheological test method, which yields high-quality results throughout the whole test. The commonly used test methods for this kind of processes are oscillatory tests with constant parameters over time or tests with constant oscillation parameters during changing test temperatures. Within food rheology such tests are used to closer looking into changing properties for example when freezing liquids to makes ice creams, when gelling liquids like milk to make cheese or when denaturising proteins while cooking eggs. The liquid state of these foods requires different test parameters compared to the gel or solid state. Oscillation parameters, which would lead to good results from the liquid state, could for example lead to the destruction of the gel structure about to be formed while on the other hand, parameters, suitable for characterizing the gel could lead to noisy data from the liquid. To overcome these contradicting requirements the classical design of a rheological test routine with fixed parameters throughout the whole test is not sufficient. A different approach to design an oscillatory test method incorporates an automatic adjustment of the test parameters during the test to stay within the optimum working range of the rheometer. When the sample is still in its liquid state and therefore does not give a sufficient response, the rheometer automatically adjusts the oscillatory parameters to achieve a better data quality. This contribution describes such test methods and shows results collected with them.

Tuesday 18:00 Marselisborg & Rosenborg

A new approach to cost-effective rheometry

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We demonstrate a novel rotational viscometer, based on simultaneous magnetic actuation and sensing and utilizing disposable probes. The probe is actuated using oscillating magnetic field and the angular displacement of the embedded magnet is monitored with a magnetic field sensor, embedded in the probe. The device was used to study aqueous solutions of glycerol (10-95 %), corresponding to a viscosity range of \sim 1 cP to \sim 400 cP.

We propose a new approach to viscosity probing. A step-stress is applied and strain oscillations are studied. Creep ringing results from a coupling between instrument's inertia, elasticity of external magnetic field, and properties of the studied fluid allowing to determine the dynamic viscosity.

The results suggest a great potential of the technique. The values computed for glycerol solutions follow the theoretical prediction based on fluid temperature, using values tabularized by Dorsey (1940).

Magnetic actuation and sensing enables application at various oscillation rates, with the speeds beyond the reach of existing high-end rheometers (up to 1 MHz), in non-contact fashion. No mechanical, electrical or optical connection between the probe and the measurement unit allows for testing of volatile/hazardous materials, under full immersion, in optically opaque fluids.

Although the cost of our measurement unit is already significantly lower than that of a classical rheometer, the true cost reduction lays in the use of disposable fluid probes. It allows for discarding the probe after each test, reducing the need for tedious, time-consuming, and therefore expensive cleaning procedures. It is worth mentioning, that a cleaning procedure bears the risk of contamination of the following sample. This error, in turn, might have serious and expensive consequences. We therefore see the future in further development of presented method.

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Tuesday 18:00 Marselisborg & Rosenborg

On the definition of the right rheological characterization protocol for complex fluids undergone to impact loads

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In the framework of '*rheo*'-inforced composites for energy dissipating systems, either with an active or passive fluid [1], it is of great importance having it characterized rheologically according to the working conditions. In spite that some of these composites are engineered for applications where sudden external mechanical loads (impacts) are applied, the fluid are usually characterized under steady state conditions by means of the apparent viscosity curve of the complex fluid embedded into the system[2].

Concentrated suspensions of precipitated calcium carbonate (PCC) in glycerol has been considered in the past as potential formulations for 'rheo'-inforcing different scaffold materials, mainly open-cell foams [3]. In this study we analyze the apparent viscosity curve obtained from transient and steady state conditions of four different concentrated suspensions of PCC particles, with different particle shapes and sizes, as well as different surface treatments, dispersed in glycerol. The obtained results show that the same suspensions may exhibit apparent shear-thickening or apparent shear-thinning depending on the 'recording-time' of the experiment, which can be justified from the transient response of the microstructure form by the PCC particles. With this work we intend to highlight the importance of defining a right experimental protocol for the rheological characterization of complex fluids formulated to be used in composites for protection applications under impacts.

[1] F.J. Galindo-Rosales. Appl. Scie., 6, 206 (2016).

[2] F.J. Galindo-Rosales, et al. Mat. & Des., 82 (5) 326-334.

[3] R.G. Egres and N.J. Wagner. J. Rheol. 49 (2003) 719-746.

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Tuesday 18:00 Marselisborg & Rosenborg

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The μ-rheometer: an effective microfluidic platform to measure the relaxation time of weakly viscoelastic polymer solutions

<u>Francesco Del Giudice</u>¹, Gaetano D'Avino², Ilaria De Santo³, Vincenzo Calcagno², Valeria Esposito Taliento⁴, Simon J. Haward⁵, Francesco Greco⁶, Paolo A. Netti³, Pier Luca Maffettone², and Amy Q. Shen⁵

¹Okinawa Institute of Science and Technology Graduate Univers, Okinawa, Japan; ²Dipartimento di Ingegneria Chimica, dei Materiali e della Pr, Universitá di Napoli Federico II, Naples, Italy; ³Center for Advanced Biomaterials for Health Care, Naples, Italy; ⁴Dipartimento di Ingegneria Chimica, dei Materiali e della Pr, Universitá di Napoli Federico II, Naples, Italy; ⁵Okinawa Institute of Science and Technology, Onna-son, Okinawa 904-0495, Japan; ⁶Istituto di Ricerche sulla Combustione, IRC-CNR, Naples, Italy

Measuring the longest relaxation λ time of a viscoelastic liquid is an important step in its rheological characterization. For very dilute macromolecular solutions, such measurement becomes challenging through conventional techniques, e.g. frequency response in linear viscoelasticity or first normal stress difference measurements. Here, we present a novel microfluidic platform, the μ -rheometer, to estimate the relaxation time of various viscoelastic fluids, down to μ -seconds. The working principle is based on the viscoelastic alignment of solid particles in a straight microchannel. In this poster, we summarize our recent findings on the measurements of λ for several classes of polymer solutions: i) Dilute polymer solutions of neutral polymers in near-theta and good solvents. We compare these results between the μ -rheometer and those obtained from an extensional flow based microfluidic platform relying on the onset of flow-induced birefringence, called OSCER. Good agreement between experimental measurements from the two platforms is found. ii) Dilute aqueous polyelectrolyte solutions, namely hyaluronic acid and chitosan, in salt-free and salty conditions. For the hyaluronic acid, good agreement is found between λ derived by using our μ -rheometer and that evaluated by fitting the viscosity curves (obtained from conventional shear rheometry) through the Bird- Carreau model. For Chitosan solutions, comparison with other techniques is not possible due to small values of λ -60 µs detected. Experimental measurements again agree well with theory. iii) Hydroxyethyl cellulose solutions in a semidilute regime. λ values derived from our μ -rheometer with those obtained through bulk and micro- rheological techniques are in quantitative agreement.

Tuesday 18:00 Marselisborg & Rosenborg

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Estimation of nominal viscosity of Newtonian liquids from data obtained by an oscillation-type density meter

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This communication evidences the possibility to use data obtained by an oscillation-type density meter, DMA 5000 M from Anton Paar, to estimate the value of the dynamic viscosity of Newtonian liquids. The viscous behavior of a liquid leads to a damping of the resonance

oscillation of an oscillation-type density meter and, thus, to a wrong density indication if not corrected. A correction can be calculated by measuring this damping which is done by measuring not only the ground oscillation but additionally a harmonic wave which is done by a DMA 5000 M. On the other hand, gives this measurement of damping the opportunity to estimate the viscosity of the measured liquid without an additional viscosity measurement. The relation between viscosity and the damping indication Q given by a DMA 5000 M was measured. The viscosity can be determined by a simple exponential equation in the damping indication range of 1100 and 3000 with an uncertainty of 10 %. This damping indication covers the viscosity range from 0.7 mPa s to 220 mPa s. If instead of the damping indication the difference between corrected and uncorrected density is used a polynomial of third order allows a determination of the viscosity with similar uncertainty. These relations might be considered being useful for laboratories that need a rough estimation of sample viscosity without having the opportunity to measure viscosity directly.

Tuesday 18:00 Marselisborg & Rosenborg

Development of RheoSpec viscometer based on EMS method

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The EMS viscometer has many advantages in liquid viscosity measurements, such as a wide range of shear rate, easy handling, low cost, contamination-free for sample and environment, and so on. This viscometer is based on the EMS (Electro-Magnetically Spinning) method, in which a metal probe in the sample liquid is driven by the remote torque generated by rotating magnetic field, and the rotational speed of the probe gives shear stress, shear rate and viscosity. We have already developed two types of EMS viscometer with different probe shapes, a sphere in the liquid and a floating disk on the liquid surface. Now we developed the third generation of EMS viscometer named RheoSpec, in which the probe is a spinning top in the liquid. One of the key features of the RheoSpec is a wider measurable range of the viscosity. Especially, it shows quite high performance for the low viscous liquids such as aqueous solutions or human blood. In addition, this method is built under the stress-control concept. We demonstrated that we can measure the high viscosity and the yield stress of pastes and distinguish the Bingham fluid and the pseudoplastic fluid clearly with the RheoSpec viscometer.

Tuesday 18:00 Marselisborg & Rosenborg

Study of a falling ball rheometer adapted to low shear stresses Patrick Ballereau¹, Daniel Truong², and Adriana Matias³

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The Joint Metrology Laboratory LNE-CNAM has studied an absolute falling ball viscometer adapted to low viscosities of Newtonian liquids up to a value of 15 mPa.s. This low viscosity requires the use of small-diameter ball (0.48 mm). The small diameter of this ball mandated the design and the construction of a gripper. This gripper uses a microsystem-specific technique: the adhesion by Van der Waals forces. The operation of this gripper is described in this presentation. Along with this work, a research regarding the use of this experimental device as a falling ball rheometer was launched. An advantage of this device is the viscosity measurement of non-Newtonian fluids at low shear stresses for the shear-thinning fluids and yield stress fluids studies. Keywords: absolute falling ball viscometer, microsystem, rheology, shear-thinning fluids, yield stress

Tuesday 18:00 Marselisborg & Rosenborg

New insights into the use of a rotational rheometer as tribometer

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A tribometer requires speed and load control as well as a force or torque measurement to acquire tribological data. An air bearing supported rotational rheometer allows the measurement of the same variables but concerning speed and torque in a broader range and with better accuracy. This fact and the intension to perform both speed and torque controlled experiments to measure Stribeck curves as well as the static friction with one single instrument led in 2006 to the idea to design a tribology attachment turning a commercial available rheometer into a high resolution tribometer based on the ball-on-three-plates principle. [Heyer P., Läuger J. (2009) Lubrication Science, 21, 253-268]. This tribometer accessory has been used extensively and a plethora of research papers have been published using the ball-on-three-plate setup. Since then the original setup has been extended into a tribometer platform including: 1. Ball-on-three-plate for a convection oven with Temperature range: -150° C - $+600^{\circ}$ C. 2. Humidity chamber with range of relative humidity: 5% to 95%. 3. Holder system for the ball-on-three-plate system with lower limit of load range of 0.03N. 4. New geometries: Pins-on-three-plates, ball-on-three-balls, rolling bearing holder, larger ball-on-three-plate geometry, holder for O-rings. 5. Pins-on-disc system with flat-on-flat, line-on-flat, point-on-flat contacts for varying surface pressures. 6. Oscillatory testing and introduction of new tribological friction moduli. The aim of this contribution is to discuss different tribological geometries and to present new results ranging from static friction measurements, Stribeck curves, and wear testing on materials as different as lubricants, bitumen, cartilage, and food under various different environmental conditions, showing the wide range of applications covered by such a type of rheo-tribometer.

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Highly conductive polymer-nanocomposites through double percolation of functionalized graphene nanosheets in a dynamically asymmetric blend

Setareh Kazem Farahzadi¹, <u>Fatemeh Goharpey</u>¹, Jafar Khademzadeh Yeganeh², and Mohammad Heydarnejad Moghadam¹ ¹Department of Polymer Engineering and Color Technology, Amirkabir University of Technology, Tehran, Tehran 15875-4413, Iran; ²Qom University of Technology, Qom, Iran

The addition of nanoparticles with a preferential affinity to the minor component into a dynamically asymmetric LCST blend of polystyrene/ poly(vinyl methyl ether) (PS/PVME), a well-known phase separating model of viscoelastic phase separation (VPS), is a potential route to induce desired phase-separating morphology This work is worthwhile considering the role of nanoparticles in arresting the transient network-like structure of VPS which is thermodynamically unstable; And at the same time reducing the electrical percolation threshold that is an important issue in nanocomposites processing. Hydrophobic graphene nanosheets, which self-assemble in the bulk of PS-rich phase (slower dynamics), had been functionalized through reacting graphene oxide nanosheets with octadecylamine and were used to control the kinetics of phase separation by slowing down (or even arresting) the domain growth and to induce high electrical conductivity through double percolation event at a very low volume fraction.

Tuesday 18:00 Marselisborg & Rosenborg

Steady-shear and viscoelastic properties of cellulose nanofibril-nanoclay dispersions

Yingxin Liu, Pierre Munier, Korneliya Gordeyeva, and Lennart Bergström

Marselisborg & Rosenborg

Stockholm University, Stockholm, Sweden

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Successful production of cellulose nanofibril (CNF)-nanoclay composite materials relies on the ability to process and assemble CNFnanoclay aqueous dispersions, with rheological properties playing a crucial role. During ice-templating processes, such as freeze-casting, the dispersion undergoes shear forces due to the formation of ice crystals growing in a specific direction. Comprehensive studies of the rheology of CNF-nanoclay dispersions are rare, and previous rheological studies were mainly centered on plate-like nanoclays and moderately charged or uncharged nanocellulose particles. In this study, we have evaluated the steady-shear and viscoelastic properties of aqueous dispersions of plate-like bentonite and rod-like sepiolite nanoparticles together with CNF of different charge densities. We will discuss how the interaction between the CNF and the amphoteric bentonite particles and the acidic sepiolite rods affects the rheological properties at different CNF/nanoclay ratios. We will show that addition of CNF above the gelation threshold (0.1 wt%) promotes breakup of the sepiolite network and assists the alignment of the rod-like particles, even at low shear rates. It will be demonstrated how control of the rheological properties and thus the microstructure of nanocellulose-based composite dispersions result in the production of low-weight foams with outstanding mechanical and thermal insulating properties.

Tuesday 18:00 Marselisborg & Rosenborg

Synthesis of hollow silica nanospheres with raspberry-like morphology by sacrificial polystyrene templates for thermal insulation applications

sadegh kazemidoust demouchali¹, Saeed Pourmahdian¹, and Behzad Shirkavand hadavand²

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The super insulating properties of hollow silica nanospheres, make them ideal candidate as potential nano insulating materials for energy efficient buildings and other applications. A small inner diameter and a thin wall thickness are generally required for hollow silica nanospheres to achieve as low thermal conductivity as possible. In this work, hollow silica nanospheres with raspberry-like morphology with a pore diameter of about 100-300 nm and a shell thickness of 10-30 nm have been prepared by using emulsion polymerization of polyacrylic acid (PAA) functionalized polystyrene (PS) followed by the sol-gel process. The size of the PS templates and shell thickness could easily be controlled by adjusting the AA/styrene weight ratio and tetraethyl orthosilicate (TEOS) concentration as silica precursor, respectively

Tuesday 18:00 Marselisborg & Rosenborg

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Rheological and electrical properties of LDPE-GnP nanocomposites Karolina Gaska, Xiangdong Xu, Rian Hafiizh Azhari, Stanislaw Gubanski, and Roland Kádár

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The high voltage direct current technology is considered as the most feasible and reliable solution for electric energy transportation across seas and inland. It is expected that the HVDC cables will be able to withstand extremely high electric stresses. However, the weakest points of the cables technology are located in terminations and joints. Therefore, a precise control of electric field distribution in these components is a crucial issue for maintaining their proper operation. For this reason LDPE filled with graphene nanoplatelets (GnP) nanocomposites were investigated as a candidate for controlling the electric field. In this study we focus on the rheological and electrical characterization of polyethylene - GnP nanocomposite for HV. A low density polyethylene (LDPE, $M_w = 91641$, PD = 7.55) filled with GnP M5 (XG Sciences) samples with 1, 3, 5 and 7.5 wt.% of filler content were extruded by means of a Brabender 19/25D single-screw extruder, equipped with conveyor belt and a conventional screw. The rheological characterization was performed on an Anton Paar MCR702 TwinDrive rheometer. Linear and nonlinear viscoelastic oscillatory tests were performed with the purpose of determining the percolation thresholds. In linear viscoelastic frequency sweeps, the percolation was detected using the storage modulus plateau recorded at low angular frequencies. FT rheology was used for nonlinear viscoelastic measurements in dynamic strain sweeps. The influence of filler content and percolation was detected using the relative third higher harmonic of the shear stress. DC conductivity was investigated using Keithley

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Electrometer, which detects current flowing through the sample. Significant reductions of the through-plane conductivity was obtained for all nanocomposites at low electric fields.

Tuesday 18:00 Marselisborg & Rosenborg

Nanocomposites based on poly(styrene-b-(ethylene-co-butylene)-b-styrene) triblock copolymer and modified graphene-carbon nanotube hybrids: Rheological and electrical study

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Novel nanocomposites based on poly(styrene-b-(ethylene-co-butylene)-b-styrene) triblock copolymer with hexagonally packed cylindrical (HEX) microdomains, and Graphene-CNT hybrids had made it possible to achieve stretchable electrically conductive materials at very low loadings of nanoadditives. organophilic graphene nanosheets had been functionalized through reacting graphene oxide nanosheets with octadecylamine. Chemical modification of MWCNTs was performed via sidewall carboxylic acid functionalization and further modification using octadecylamine. Effective functionalization of nanoparticles was characterized by means of FTIR ,XRD,FE-SEM and TGA. Nanocomposites were prepared by solution mixing. Appropriate surface modification of hybrid components results in well dispersion of nanoparticles, due to formation of 3-Dimensional network of nanoadditives. Rheological measurements were also used to determine the effect of hybrid nanoparticles on micro phase separated structures, orientation and recovery of cylindrical PS domains. Electrical conductivity measurements using CNT and Graphene simultaneously, demonstrates synergistic transport effect due to Graphene-CNT-Graphene physically interconnected conductive network structure formed throughout the matrix.

Tuesday 18:00 Marselisborg & Rosenborg

Time-dependent properties and microstructure in colloidal dispersion

Roberta Massaro¹, Christian Clasen², and Peter Van Puyvelde³

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The balance of hydrodynamic and interparticle forces determines the microstructure and the macroscopic behavior under flow in nanocomposites. Flow can induce structural changes which manifest in a variable viscosity. If the changes are reversible and time dependent, the effect is called thixotropy. The time scales associated with this structuration are typically slower than the classical viscoelastic time scales of the components but faster than the slow phenomena due to ageing or degradation. A proper understanding of the thixotropic flow characteristics allows to solve complex industrial problems. By using different types of model particles in polymeric media of different rheology, we can probe the effect of varying particle-particle and particle-matrix interactions on the thixotropic behavior. In addition, gradually changing the molecular weight of the matrix allows us to study the competition between the time scale associated with the inherent viscoelasticity of the matrix polymer. As such, we are able to develop a rationally based general understanding of the structure development in nanocomposites.

Tuesday 18:00 Marselisborg & Rosenborg

Toward a comprehensive drag closure for inhomogeneous dense suspensions

<u>Ahmadreza Rashedi¹</u>, Sarah Hormozi², and Guillaume Ovarlez³

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Dense suspensions of non-colloidal particles exhibit novel features. In a nonhomogeneous shear flow, it is observed that particles migrate from the high shear rate region to the low shear rate region. This phenomenon is called Shear-Induced Migration (SIM). The Suspension Balance Model (SBM) of Nott and Brady (1994) has been taken as an approach to model SIM. Where the SIM is attributed to the diffusive fluxes that arise naturally from gradients in the particle phase stresses. However, there are still unanswered questions and an ongoing debate on the nature of particle stress in the dense suspensions. Recent experiments show that the SBM not only fails in predicting the steady state distribution of particle phase in flows of dense suspensions but also fails in predicting the kinetics of the SIM. In addition, recent theoretical works question the derivation of the SBM and the simple supposition of drag closures in inhomogeneous flows of dense suspensions. We have designed and built an original setup to revisit available drag closures via performing well-resolved experiments. We present our preliminary results of a drag closure taking into account inhomogeneities of the solid phase volume fraction and the shear rate. Nott PR, Brady JF, Pressure-driven flow of suspensions: simulation and theory. J Fluid Mech 275 (1994). Lhuillier (2009), Nott et al. (2011), Snook et al (2015)

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Use of rheological models for the evaluation of cement pastes with air-entraining agent in different temperatures

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Despite the air-incorporation improve the workability and productivity of cementitious materials, making them more sustainable, it can become very sensitive to extrinsic factors, like processing and environmental conditions. Therefore, the correct evaluation of the rheological

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properties is extremely important for an understanding of the main causes of use of air-entraining agents (AEA) in these compositions. Tests with variation in the shear rate are commonly used, and the results are often evaluated applying rheological models to quantify both the yield stress and the plastic viscosity of these products. The most commons are Herschel-Bulkley, Casson or Bingham, but in many cases the models applied do not correctly represent the results obtained, do not fitting to a reality observed in everyday life. So, in this work the rheological properties of cement pastes with air-entraining agents were quantified at different temperatures, and applied rheological models to evaluate the relationship between the results that was measured and modeled. The main conclusions were that the use of AEA and the temperature affected the rheological properties, the temperature affected in the air-incorporation and, the application of rheological models does not well represent that have been measured, mainly in extreme shear rates.

Tuesday 18:00 Marselisborg & Rosenborg

The effects of electrode geometry, particle size and operation frequency on the collection pattern of latex particle under electroosmosis

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Electroosmosis is a convenient method to collect small size particles or cells. Many factors like surface charge density, applied frequency and electrode geometry might affect its performance. A complete study on these factors might illuminate which factor is critical. The electroosmosis microfluidic is made of two parallel electrodes separated by a spacer. The chip consists of a top transparent ITO electrode and a bottom electrode separated by a curing PDMS spacer. The bottom electrode is made of Corning 1737 glass with different sputtered Cr pattern and uses the photoresist as dielectric layer. The amine-modified polystyrene particles with different size were collected by varying frequencies. The effects of electrode geometry, particle size and frequency were investigated by numerical simulations with a commercial software Comsol under multi-physics modelling. The mechanisms are investigated by parameter study. The results indicate the geometry of electrode is the least significant factor compared to frequency or particle size. Meanwhile, frequency is a dominant factor in collection pattern. For low frequency 100 Hz, the particles are accumulated in the peripheral area. Meanwhile, for high frequency 1000 Hz, the particles are accumulated in the center region of the bottom electrode. The particle size effect is primarily affected by the applied frequency. For low frequency 1000 Hz, the combined effect with electroosmosis and dielectrophoresis affects the collection pattern. These results are validated through numerical simulation where the frequency and particle size are considered. In conclusion, the electrode geometry is not a prominent factor compared to frequency and particle size. The collection pattern is affected by particle size which is also frequency dependent.

Wednesday 14:20 Marselisborg & Rosenborg

The effect of mud contamination on the properties of a G-type cement slurry

<u>Aikaterini Biotaki</u>¹, Dimitrios Marinakis², Maria Kompitsaki², Stylianos Mavrigiannakis², and Vassilios C. Kelessidis² ¹Petroleum Engineering, Technical University of Denmark, Copenhagen, Denmark; ²School of Mineral Resources Engineering, Technical University of Crete, Chania 73100, Greece

Cementing is a crucial stage of wellbore completion. A primary cement job aims to ensure complete downhole zonal isolation. For optimal cement slurry placement, the drilling mud must first be efficiently and fully displaced. However, in many cases the mud displacement is incomplete resulting in mud contaminated cement, which can be detrimental to the cement integrity. When mud contamination occurs, slurry's properties deteriorate significantly. Although this effect is already acknowledged, and several methodologies have been developed to prevent it, full understanding and quantification of the mud contamination detrimental effects on slurry's rheological properties and strength is not available to date. In this work, a quantitative approach was conducted to assess the bentonite mud contamination effect on the cement slurry's properties. Mud and cement slurry samples were prepared as per API procedures but in atmospheric conditions. Special care was given to the mixing procedures of the mud-cement samples in order to best simulate the downhole borehole conditions. Two different mixing procedures were applied, one resulting in a more homogeneous mixture, while the mud concentrations on the cement investigated ranged from 5% to 25%. The rheological properties of the contaminated slurries were studied at two different temperatures, while the final cement strength was also examined. The results indicate that the mixing procedure greatly affected the properties of the slurry-mud mixture. For heavily contaminated samples, the shear stresses increased at all shear rates, while time had also a big effect. Temperature decreased the shear stresses, albeit at a smaller rate than if no contamination was present. High mud concentration reduced significantly the slurry's flowability resulting to a material with plastic behavior. Unconfined Compressive Strength (UCS) values were lower for the heavily contaminated samples, while in the case of less homogeneous mixtures they were widely distributed for same composition samples.

Wednesday 14:20 Marselisborg & Rosenborg

Physical stability of structured fluids containing air bubbles

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Home-care products are detergent systems that differ for applications, formulation and structure. From a physical point of view, detergents are usually suspensions where a surfactant-based, worm-like micellar solution represents the continuous phase and colloidal fibers are added in order to provide the matrices of specific properties, e.g. the ability to suspend pigments, oil droplets, perfumes. In spite of the many advantages assured by the presence of the fibers in terms of shelf life, the resulting system can be mechanically unstable. Basically, the main responsible for this instability is the load applied by air bubbles, which are found into the final product, due to the process itself.

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We studied various samples, which differ from each other for aeration level and fiber concentration. The rheological behavior and the microstructure of these fluids has been characterized. In parallel, a time lapse photography technique has been used to monitor the time evolution of the air bubbles trapped in the fluids. The motion of single bubbles as well as the cooperative motion of bubble ensembles have been analyzed to verify the possibility of microstructure collapse. We found that fiber concentration, which dictates the yield stress of the fluid, aeration level and temperature can influence the stability of the final product. In particular, under given conditions, bubbles can apply a remarkable load on the fiber network during their buoyancy-driven rise, thus inducing the collapse of the structure. The result is a clear phase separation, with the matrix without fibers standing on the bottom of the fluid volume, while a more concentrated system is moving towards the free surface. Data have been collected, critically analyzed and compared with theoretical predictions and simulation model made by Comsol Multiphysics software.

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Enhancement of Drilling Fluid Rheology by Nanoparticles - A Solution Key to Most Drilling Problems Mortatha S. Alyasiri¹, Dongsheng Wen², and Joseph S. Antony³

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The development of new oil production techniques such as long deviated wells and drilling in ultra-deep water imposes the required performance of the drilling fluids continue to rise. As well, the drilling fluid movement cycle is often unstable; mutually changes between a movement and a steady state. Hence, the challenge is to design a single recipe of drilling fluid that display agreeable abilities both at rest and in dynamic. Seeding nanoparticles into a drilling fluid is a promising technique that could solve some problems associated with drilling operations. However, current studies are insufficient, and still in its infancy, with many inconsistent results. The paper aims to explore and assess the influence of various nanoparticles and their mixtures on the rheological properties of water-based drilling fluids. A number of nanoparticles based water based drilling fluids was formulated and their rheological properties were examined by an Anton Parr rheometer. The results show that the addition of nanoparticles increased the performance of WBM both at stationary and dynamic conditions. In addition, these nanoparticles increased the degree and the speed of the structural recovery by reducing the relaxation time, which is desirable to prevent the sedimentation of the cuttings and weighting materials. Among all the particles examined, a mixture of Gr-Al2O3 nanoparticles showed the best rheological results.

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Tailoring the flow behavior of coke water slurries for entrained flow gasification

Leon Jampolski¹, Alexander Sänger², Tobias Jakobs², <u>Steffen Recktenwald</u>¹, Thomas Kolb², and Norbert Willenbacher¹ ¹Institute for Mechanical Process Engineering and Mechanics, Karlsruhe Institute of Technology, Karlsruhe, Baden-Württemberg 76131, Germany; ²Institute for Technical Chemistry, Karlsruhe Institute of Technology, Karlsruhe, Germany

The bioliq-process developed at KIT allows a conversion from raw biomass to carbonaceous chemicals or fuels. Coke slurries play a key role in this process. Therefore, the influence of particle size and shape on slurry viscosity was investigated using two different coke feedstocks (wheat straw (WS) and beech wood (BW)) with almost similar particle size distributions ($d\approx 20\mu$ m). Particle size and shape were modified through variation of time interval the coke was treated in a ball mill. Circularity was chosen as shape parameter and determined via image analysis. Milling results in a decrease of particle size for both feedstocks and the circularity of coke particles from WS increases while the shape of the BW particles essentially remains unaffected. At the same time the viscosity of slurries from WS decreases with increased milling time whereas the viscosity of the slurries from BW remains unchanged and we conclude that particle shape but not size is relevant for the viscosity of these slurries in storage tanks. Suppression was achieved using the capillary suspension phenomenon. Therefor a small amount of a second immiscible fluid is added, resulting in a formation of a sample-spanning network controlled by capillary forces between the particles inferred from the secondary fluid. The low shear viscosity was orders of magnitude higher than that of the native slurries, while the viscosity at high shear rates was nearly unaffected. Furthermore, atomization experiments of the stabilized slurries resulted in a substantial decrease of the droplet size at low gas to liquid ratio compared to the non-stabilized systems and this is attributed to the reduction in surface tension coming with the secondary fluid. Moreover, the spray pattern is affected by this innovative formulation concept and a transition from flapping to pulsing mode is observed resulting in a reduced spray angle.

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Insight into non-linear Rheology of highly filled non-Brownian Suspensions

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Highly filled dispersions exhibiting a yield stress and subsequent strong shear-thinning find wide industrial applications ranging from metallization pastes in Electronics and Communication to personal hygiene and food products. In most cases the yield stress is a desired feature that imparts important processing behavior or lends the products their distinct consumer perception quality. In other cases, the yield stress poses a challenge for processing and should be managed accordingly. Highly filled suspensions in viscoelastic media are particularly challenging seen from a rheological characterization perspective. To understand how these materials behave one needs to study various linear but also non-linear viscoelastic material functions as well as short time recovery behavior. These suspensions are notorious for slip, elastic flow instabilities, non-homogeneous flows (shear banding) and they are thixotropic. Slip, elastic flow instabilities and shear banding need to be mitigated in good rheological experimentation, however may also provide valuable information about material behavior. The

thixotropic nature of these materials poses yet another characterization challenge. Its impact on the measurement needs to be understood, appropriately managed, and it also is important with regards to material behavior. This paper presents examples that are taken from work on food products to metallization pastes and thermal interface materials and we also demonstrate how novel analysis schemes and ideas from design optimization are implemented to shed new light on the rather complex material behaviors that can be observed and how these relate to formulation on one and to processing on the other hand.

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Suspension rheology formulation using an Eulerian multi-fluid approach in commercial CFD software Nathanael J. Inkson

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We have adapted a well-known constitutive relation for suspension rheology by Morris and Boulay and reformulated the equation into an Eulerian multiphase finite-volume solver within the framework of a commercial Computational Fluid Dynamics code STAR-CCM+. We apply the resulting model to a variety of experiments and show that it is very successful in predicting the evolution of volume fraction profiles of the particles caused by suspension pressure due to the particle collisions which are entirely captured by the stress formulation with minimal fitting. We have considered the flow of neutrally buoyant monodisperse particles at low Reynolds number in the following geometries for validation of the model: Flow in a Couette device, pressure driven flow down a pipe and flow in an asymmetric channel bifurcation in 2D and 3D. We find excellent agreement with velocity and volume fraction profiles in all of the comparisons with experimental data without much further numerical fitting beyond the original model.

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Dramatic influence of anisotropic interactions on short time diffusion and arrest of protein solutions <u>Jin Suk Myung</u>, Peter Schurtenberger, and Anna Stradner

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In a dense and crowded environment such as the cell, an individual protein feels the presence of surrounding proteins. It is thus expected that direct and hydrodynamic interactions will strongly affect the diffusion of proteins. Examples are suspensions of eye lens proteins, where dramatic slow down of local short time diffusion of ?B-crystallin and dynamical arrest is observed experimentally under crowded conditions [1]. Here we demonstrate that an application of colloid models, together with appropriate theoretical and simulation tools that allow to incorporate direct and hydrodynamic interactions, provides detailed insight into the dynamics of protein solutions. The hybrid simulation approach combines the multiparticle collision dynamics (MPC) method for the fluid, with molecular dynamics simulations (MD) for the globular proteins [2]. We present results for the short time diffusion of different model proteins, where their dynamics are analyzed together with structural properties. The effect of hydrodynamic interactions as well as anisotropic attractions between colloids are discussed. We in particular highlight the dramatic effects of weak attractive interactions known to exist between many globular proteins on the short time diffusion provides important insight into the different mechanisms responsible for the formation of an arrested glass at high protein concentrations.

References: [1] S. Bucciarelli, J. S. Myung, B. Farago, S. Das, G. A. Vliegenthart, O. Holderer, R. G. Winkler, P. Schurtenberger, G. Gompper, A. Stradner, Sci. Adv., accepted (2016) [2] G. Gompper, T. Ihle, D. M. Kroll, R. G. Winkler, Adv. Polym. Sci. 221, 1 (2009)

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Rheology of industrial plastisol formulations

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A plastisol is a suspension of PVC particles and mineral fillers in a liquid phase composed of plasticizer and adjuvants. Interactions between components make them a unique kind of suspensions. Simplified formulations have been selected containing three types of PVC resins (with polydisperse, bidisperse and monodisperse particle size distributions) and calcium carbonate fillers of different sizes. The shear rheology has been investigated on a wide shear rate range using Couette and capillary rheometers. A nice consistency between both measurement methods is shown. The polydisperse formulation displays a shear-thinning behavior in the whole shear rate range and exhibits yield stress; the monodisperse formulation shows a shear thinning behavior at low shear rate followed by a Newtonian plateau, then a more or less pronounced dilatancy peak followed by a second shear thinning zone. A bidisperse resin stands in between. Substituting small filler particles to the PVC particles in the bidisperse formulation increases significantly the viscosity in the low shear rate range and shear thickening effects at intermediate shear rates decrease or even disappear. Different capillary diameters have been used for the rheology measurements at high shear rates. For the smallest diameter an important flow rate increase has been observed which could be explained by the occurrence of slip velocity. It has been identified using a numerical method accounting for the non monotonous behavior of the plastisol. A first approach of the elongational viscosity has been carried out using a modified Cogswell method. A very important ratio between elongational and shear viscosity is pointed out (a factor 40 instead of the Trouton ratio of 3). Some of these results may be explained on the light of the abundant literature on suspensions. Some others, as for example the shear thinning behavior at high shear rates, need further experiments and explanations.

Wednesday 14:20 Marselisborg & Rosenborg Steady and transient rheology of Graphene Oxide dispersion

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Graphene Oxide (G-O) dispersions in water are aqueous suspensions containing chemically modified graphene sheets. G-O sheets or aqueous G-O dispersions have found applications in hydrogen storage, sensing, and biomedical devices. Understanding the rheological behavior of aqueous (and other) G-O dispersions is fundamentally interesting and important for various processing operations. However, conflicting information of rheological behavior of G-O dispersions was reported in the literature. In this work, we present experimental results from shear and transient rheology of aqueous G-O dispersions at mass concentrations (0.004 wt% < c < 0.4 wt%) by using a stress-controlled rheometer. Bulk rheology measurements were conducted with glass parallel plates, steel parallel plates, and Couette geometries, to study the effect of fixture materials, spatial confinement, and fluid dynamic conditions. At c = 0.4 wt%, and at imposed stress greater than 0.8 Pa, good agreement is found between viscosity evaluated from both steady shear and transient measures, while at imposed stresses below 0.8 Pa, viscosity values significantly differ. In particular, strong oscillations in the transient viscosity are observed as a function of time. This behavior suggests the presence of yield stress is found for c > 0.04 wt%. Moreover, we find that the confinement of parallel plates does not play a significant role on the G-O dispersion rheology. In contrast, the fixture material slightly affects the rheology at high G-O concentration. By using the Couette geometry, a flow-induced instability is observed at various imposed stresses. In particular, the presence of bands along the azimuthal direction (i.e., orthogonal to the flow and the shear direction) is found. The band thickness increases with the increasing applied stress.

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Effect of shear and extensional viscosities on wet-spinning of cellulose nanofibril hydrogels

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Wet-spinning has been proposed as a method to align cellulose nanofibrils (CNF) and thus achieve novel renewable materials that fully capitalise on the strength of individual CNF. In order to upscale this technique, the spinnability of a particular CNF dope needs to become predictable through a simple experimental procedure [1]. For this purpose, we propose associating the shear and extensional viscosity of the dope with the properties of a filament wet-spun from the same dope. We have established an optimum level for the shear and extensional viscosity as well as the storage and loss moduli for wet-spinning of a CNF hydrogel. Furthermore, we present an alternative method that enables wet-spinning of CNF hydrogels even with inappropriate rheology. This method capitalises on polymer solutions with higher extensional viscosity than CNF suspensions. When this kind of solution was spun together with CNF dope into a core-shell type of composite filament, the more extensionally viscous dope acted as a supportive shell for the filament during the spinning process. Inside the shell, CNF filament could even be drawn and collected continuously (Figure 1) even though its own extensional viscosity would be insufficient for that.

[1] Lundahl, M. J.; Cunha, A. G.; Rojo, E.; Papageorgiou, A. C.; Rautkari, L.; Arboleda, J. C.; Rojas, O. J. Strength and Water Interactions of Cellulose I Filaments Wet-Spun from Cellulose Nanofibril Hydrogels. Scientific Reports 2016, 6, 30695.

Wednesday 14:20 Marselisborg & Rosenborg

Rheology of CO₂-CH₄ hydrates measured in a concentric pressure cell

PO117

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Injection and storage of CO2 in the subsurface is a highly relevant method of reducing the climate gas emissions to the earth's atmosphere. Depleted hydrocarbon reservoirs and saline aquifers are targeted as potential storage sites. In this context, a high injectivity of CO2 is critical in order to take advantage of the full storage capacity of the reservoir. Reported mechanisms causing loss in field injectivity near the CO2 injection wells are hydrate formation and salt precipitation. Hydrates form at high pressure and low temperature, and may lead to increased flow resistance and complete plugging. Typically, the injected CO2 contains a fraction of CH4 causing the temperature range in the hydrate stability zone (HSZ) to increase. To mitigate these injectivity challenges, this study systematically investigates the rheology of hydrate slurries at realistic downhole conditions.

We successfully formed and dissociated gas hydrates in a concentric cylinder pressure cell. Viscosity profiles captured the nucleation, growth and agglomeration of the hydrates. A decay in viscosity ascribed to hydrate redistribution and hydrate maturation followed the initial viscosity peak. In the presence of hydrates, flow curves were established for a wide range of shear rates. The hydrate slurries were consistently shear-thinning and demonstrated hysteresis effects. Measured yield stress gave valuable insight in hydrate agglomeration during operational stops. Hydrate dissociation occurred by thermal stimulation and was validated with a thermodynamic modeling tool.

This rheological study adds important knowledge to the field of carbon capture and storage (CCS), and in particular the transport and injection of CO2 in the presence of water. The experimental results can be used in numerical scenarios for improved prediction of CO2 flow behavior in the HSZ. We find that the combination of a modular compact rheometer, a grooved bob, and a pressure cell with thermal regulations is well suited for characterization of gas hydrates.

Wednesday 14:20 Marselisborg & Rosenborg

Effects of Preconditioning and Ageing on Rheological Properties of Model-Drilling Fluids

Benjamin Werner¹ and Bjørnar Lund²

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Many drilling fluids are thixotropic, meaning that viscosity decreases with time when subjected to shear. Other fluids may show antithixotropic (rheopectic) behavior, i.e. viscosity increase with time when subjected to shear. In both cases it is important to have a consistent procedure for how to treat the fluids prior to rheological measurements. This is vital in order to be able to compare measurements of different samples, with different instruments and between different laboratories. In the oil industry, the ISO 10416/ISO 10414-1/2 standards are used for determination of viscosity and gel strength of fluids by use of direct-indicating viscometers (Fann 35 viscometers). However, these standards do not specify in detail how the fluids should be pre-treated before measurements. Further, if results from Fann 35 viscometers are to be compared to measurements done on a rheometer, it is even more important to have a consistent pre-treatment of the fluids before the measurements. A systematic study is performed in which the effects of pre-shearing and ageing history on the rheological measurements of model drilling fluids are investigated by using a Fann35 viscometer and an Anton Paar MCR 302 rheometer. The results demonstrate the importance of consistent preconditioning of fluids before measurements. A test-procedure standard is proposed, enabling higher measurement precision and comparability of rheological measurements.

Wednesday 14:20 Marselisborg & Rosenborg

The Application of Process Tomography for the In-line Measurement of Rheology

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Tomographic measurements uncover information about the nature and distribution of components within a process media via the acquisition of signals obtained from sensors located on the periphery of the subject domain i.e. a pipe. In this paper, via a measurement of the distribution of electrical properties of process media, using Electrical Resistance Tomography (ERT), coupled with time-spaced analysis, it has been possible to extract flow and rheological parameters. This affords the production of both in-line and vessel-based velocimeters with the ability to elucidate the rheology of concentrated opaque mixtures.

Within this investigation, a multi-plane ERT system permits the determination of a time delay between acquired measurement signals and hence the determination of velocity. A non-linear regression method can then be applied to the resultant velocity profile, affording the inline determination of rheological and flow parameters of complex fluids. The determination of rheology from a velocity profile not only permits a measurement without the requirement of sampling, but also affords advantages over conventional rheometers due to its ability to extract data at very low shear rates.

Preliminary studies involved the investigation of the technique utilising fluids with known constitutive properties with the aim of ensuring a reliable and accurate velocity profile is able to be extracted. From such experimental measurements, the system has been able to be optimised to determine rheological parameters at an accuracy of $\pm 2\%$, with a variability of the system, at a maximum of $\pm 5\%$ across both Newtonian and non-Newtonian fluids. It is evident that the obtained rheological parameters. Furthermore, this analysis may be conducted without regression to specific constitutive equations, permitting the investigation of fluids of unknown rheological properties.

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Kinetics, structure and elasticity of binary thermoresponsive microgel networks

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Thermoresponsive colloidal microgels have frequently been studied in order to probe their tunable interaction potentials and their rich phase behaviour. The thermoresponsivity of these microgels allows for switching between swollen, soft repulsive and collapsed, hard attractive particles. This leads to interesting phase behaviour that encompasses a spinodal decomposition and subsequent arrest, leading to an elastic network. Here we now extend the study to binary mixtures, using particles of different sizes and transition temperatures, yielding a phase diagram of several interesting and novel phases. One such phase is the decorated gel network - upon heating, one particle type forms a network, and after further heating the second particle decorates the already present particle network. The resulting network structure depends strongly on the heating method, and evolves from a regular decorated network for slow heating to a randomly collapsed mixed network for a fast heating process, with dramatic changes in the mechanical properties of the gels. Using frequency-dependent and timedependent rheology, light scattering methods and confocal microscopy, we probe the elasticity and the related local and global network structure of the system as a function of temperature and heating method.

An increase of magnetic fluid viscosity1 in a magnetic field (the magnetorheological effect) was experimentally discovered in the 1950s for systems based on iron carbonyl and iron oxide2. The aim of this work was to study the concentration dependence of the effect of permanent magnetic field strength on the viscosity of an iron-aerosil-glycerol magnetorheological suspension under the conditions of a rotational flow. A suspension of silica and iron nanoparticles in glycerol was studied as a magnetic fluid. Iron nanopowder (weight-average particle diameter of 150 nm) and colloidal silica (weight-average particle diameter of 250 nm) were used. Suspensions were prepared by mixing

The Effect of a Magnetic Field on the Rheological Properties of Iron - Aerosil - Glycerol Suspensions

Wednesday 14:20 Marselisborg & Rosenborg

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glycerol with aerosil nanoparticles. The concentration of silica nanoparticles in the system was constant and equal to 10 wt %. Dispersions of iron nanoparticles were prepared by adding them to the suspensions. The viscosities of the dispersions were measured us in a Rheotest RN 4.1 under magnetic fields with the strength of 290 kA/m and field lines directed perpendicularly to the rotor-rotation axis and with the strength of 280 kA/m and field lines directed parallel to the rotor-rotation axis. At a low shear rate (0-2 s-1), the effect of a magnetic field on the suspension viscosity dominates over the effect of a mechanical stress field, and the viscosity increases by more than 40 times. In this case, the field oriented perpendicular to the rotor-rotation axis affects the system viscosity four times as strongly as the field oriented parallel to the rotation axis does. At a high shear rate (15 s-1), the effect of the mechanical stress field prevails, viscosity increases by a factor as small as 1.4. At the same time, the direction of the field lines has in fact no effect on the viscosity. Thus, the boundary conditions of the influence of the magnetic and mechanical fields on the rheological properties of ferrofluids have been determined that may be used in the technology of new magnetosensitive nanomaterials.

Wednesday 14:20 Marselisborg & Rosenborg

Discontinuous shear thickening in the presence of superplasticizer molecules

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The superplasticizer molecules are polyelectrolytes which are used in cement industry to increase the maximum volume fraction of mineral particles still keepeing a low viscosity. The high volume fraction which can be attained thanks to these molecules favors the onset of the discontinuous shear thickening transition (DST) and we found that it was the case with gypsum, calcium carbonate and iron particles. We studied both experimentally and theoretically the effect of different superplasticizer molecules on the critical stress associated with the onset of DST. For all the combinations of particles and superplastifier the DST transition was quite different from the one observed on other systems. Instead of the usual "S shape" for stress versus shear rate in a controlled stress experiment an abrupt decrease of shear rate was observed followed by a regime of strong oscillations of the shear rate whose average value remains approximately constant as long as the particles are not expulsed from the liquid phase. The difference in the critical stress between different polyelectrolytes and/or particles will be discussed with the help of a model taking into account the density of the adsorbed polymer layer and its thickness. Above the transition and at a constant imposed stress, a regime of regular oscillations of saw tooth shape with a sharp decrease of shear rate accompanied by a pulse of normal force was followed by a more chaotic regime at higher stress. The average strain corresponding to one period was almost constant and close to unity but the frequency of the oscillations was increasing with the applied stress. This regime will be analysed with the help of a viscoelastic model taking into account the inertia of the tool and the change of the shear modulus and viscosity with the fraction of frictional contacts.

Wednesday 14:20 Marselisborg & Rosenborg

Multiscale Modelling of Non-Spherical Particle Suspensions: Confinement and Inertial Effects

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Flows of fibre-reinforced composite materials and suspensions of non-spherical particles (ellipsoids, cylinders, etc) are often described using phenomenological adaptations of the classical Jeffery model, which predicts the evolution of the orientation of a rigid ellipsoid immersed in a Newtonian fluid in a Stokes flow field. Amongst other limitations, such models neglect the mass of the suspended particles, and therefore the induced inertial effects. In addition, these models address unconfined flows, despite the fact that processes of industrial interest often involve narrow gaps where fibres may have length greater than the gap and wall effects cannot be ignored. In this work, we survey on the one hand the impact of inertial effects on the fibre orientation kinematics, and on the other hand we extend our previous study on confined fibre suspensions [1] using a phenomenological approach inspired by plasticity theory.

Reference: [1] A. Scheuer, E. Abisset-Chavanne, F. Chinesta, R. Keunings, Second-gradient modelling of orientation development and rheology of dilute confined suspensions, Journal of Non-Newtonian Fluid Mechanics, 237, 54-64 (2016)

Wednesday 14:20 Marselisborg & Rosenborg

Tridimensional Rheological Characterization of Magneto Rheological Fluids

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Typically, the standard measurements of Magnetorheological fluids apply vertical magnetic fields versus the applied shear. In the present work, it will performed oscillatory measurement in several directions versus the applied magnetic field. The main target is, from a practical point of view, to stablished the relationship between the rheological properties and the magnetic field applied not only in the perpendicular direction but also in the other 2 spatial directions. In order to get that target, Plastic Orthogonal superposition geometry has being build. This geometry allows us to perform several kinds of shear stresses: s12, s32, s23

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Wednesday 14:20 Marselisborg & Rosenborg Experimental study of filament break-off of dense suspensions

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The precise and repeatable deposition of functional fluids is increasing in importance in areas such as pharmaceuticals, digital printing, electronics production et cetera. The rheological characteristics of the functional fluids of interest in these different areas vary radically with respect to viscosity, material loading and viscoelastic properties. As with the jet printing of dyes and other low-viscosity fluids, the jetting of dense fluid suspensions is dependent on the repeatable break-off of the fluid filament into well-formed droplets. It is well known that the break-off of dense suspensions is dependent on the volume fraction of the solid phase, particle size and morphology, fluid phase viscosity et cetera, see for example van Deen et al. (2013). The purpose of this study is to establish a deeper understanding of the break-off process of filaments of dense suspensions. The experimental set-up consists of a filament break-off device (FilBO) developed in-house. A cylindrical sample (d_cyl = 1 mm and h_cyl = 1 mm) of the suspension is extended using a cylindrical probe travelling between v_cyl = 100-800 mm/s in the vertical direction. The suspension samples consist of a resin-based flux and spherical particles with diameters of d_p = 10-25 μ m. The size distribution of the particles is approximately Gaussian with a diameter deviation of s_{d_p} = 0.20 • d_p. A decrease in particle size correlates with increasing break-off length. Further results relating break-off times which correlates with higher satellite levels and poorer dot shape when jetted onto a substrate. Suspensions within a certain break-off time range show optimal jetting results. This implies that filament stretching of dense suspensions can be connected to their jetting behaviour, potentially allowing for this technique to be used to predict jetting results.

Wednesday 14:20 Marselisborg & Rosenborg

Impact of packing particle in the rheological properties of cementitious pastes additive with polycarboxylate

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Formulations of low binder concrete have been an alternative for reducing the environmental impact of the cement production chain. To this, the use of superplasticizers to reduce the water demand, and the implementation of packing particles concepts are essential tools. At the same time that the optimization of packing results in lower need of water to recover the particles, the steric stabilization promoted by the use of superplasticizer is responsible for improving the workability for long time. However, the effects of packing particle associated with additive in the rheological / chemical reactions are still poorly understood, deserving deep investigations. At this way, the main purpose of this work was to evaluate the impact of packing on the particles mobility during the flow (using an interference model) and the chemical reaction of compositions formulated with Portland cement and limestone filler. The binder content was kept constant and the superplasticizer optimized. Chemical reaction was monitored by isothermal conduction calorimetry and the rheological properties by rotational and oscillatory rheometry. The results show the reduction in the yield stress and viscosity in function of improvements of packing particle, alteration in the gain on the consistency over time and changes in the chemical reaction.

Wednesday 14:20 Marselisborg & Rosenborg

Characterization of Printing Pastes using the Pendant Thread Approach

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Industrial silicon solar cell metallization is still dominated by screen printing technology. On the front surface, highly developed silver pastes are printed, dried and sintered subsequently forming a robust grid structure of reliable contacts with proven long term stability. Despite high yield stresses, also the surface tension becomes relevant when printing finest contact fingers. Hence a setup called pendant thread was developed that allows for the extraction of both, a dynamic extensional yield stress and the surface tension of applied silver pastes. Similar to the pendant drop, a pendant thread is formed by dispensing the respective paste through a certain nozzle at very low speeds while measuring the thread diameter D. Once gravity and surface forces acting on the thread become larger than the extensional yield stress $s_{-}(y,e)$, the thread starts to neck and the isolated bottom part eventually drops on a micro scale. A force balance in the thread when necking is initiated reveals:

 $m_c g + GpD = s_c (D^2 p)/4$

Solving for the normal stress in the thread gives:

 $s_z = 4 (m_c g)/(pD^2) = s_(y,e) - 4 G/D$

By varying D and performing a linear fit to the obtained data points, $s_{(y,e)}$ and G can be extracted. A comparison with shear yield stress data revealed that the obtained values for Ag-printing pastes are in a similar range when considering the von Mises criterion, same accounts for the surface tension that was compared with the value of the pure solvent extracted with the pendant drop approach. With this approach it could further be demonstrated how &sigma_y depends on the apparent shear rate inside the nozzle by varying the paste velocity at the

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nozzle outlet. This dynamic yield stress $s_{y,e} = f(d?/dt)$ was fitted using a Power Law approach within three magnitudes of shear rates. In the meantime, various pastes have been characterized under different conditions using the pendant thread approach and corresponding results will be presented.

Wednesday 14:20 Marselisborg & Rosenborg

Flow-induced structural orientation and relaxation in blends from biobased polylactide and liquidcrystalline polymers

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Bio-based composite materials with enhanced properties have the potential to replace fossil-based polymers. Polylactic-acid (PLA) is a promising candidate for self-reinforced composites due to its tunable melting range [1]. However, for enhanced mechanical performance also additional reinforcement via blending with thermotropic liquid-crystalline polymers (TLCP) can be beneficial [2,3]. The effects of flow on the micro- and mesoscale structure need to be well correlated with chemical composition, capillary number concepts, and processing conditions.

In this study, we investigate for pure and blended TLCP-PLA the effects of shear deformation and rate on the morphology by combined Rheo-Optics and Rheo-Scattering. Polarised Optical Microscopy (POM) in addition to a shear rheometer and shear-cell setups shows that the threaded morphology on a mesoscale breaks and orients along the flow direction under continuous flow, but reforms during relaxation. The molecular orientation during and after shear, respectively, is probed via a combination of rotational shear rheometry with synchrotron wide-angle X-ray diffraction analysis (WAXD). The acquired orientation as determined by the orientation factor along the azimuthal intensity distribution is found to be directly related to the shear strain, but hardly to the shear rate, and also vanishes within few minutes with flow cessation and relaxation. The results provide detailed insights into the structure evolution of the individual polymer phases as a function of flow profiles as well as material parameters.

[1] Mai F., Tu W., Bilotti E., Peijs T. Comp. Part A: Appl. Sci. Manufact. (2015) 76, 145

[2] Wilsens C., Pepels M., Spoelstra A., Portale G., Auhl D., Deshmuk Y., Harings J. Macromol. (2016) 49, 2228-2237

[3] Wilsens C., Verhoeven J., Noordover B., Hansen M., Auhl D., Rastogi S. Macromol. (2014) 3306

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Wednesday 14:20 Marselisborg & Rosenborg

Microfluidic Visual Rheometer

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Rheological analysis is made fast and easy with a novel instrument based on a microfluidic flow comparator. The technology allows flow viscosity measurements of liquid products from water-like inks to thick cosmetic formulations, under a wide range of shear rates (up to 10^{5} s-1). This user-friendly principle makes possible routine visual control of samples and flow cells to assess measurement quality.

A sample and a viscosity standard are pushed together through a microfluidic comparator (Y-junction) at controlled flow rates set by syringe pumps. As a result, a laminar co- flow can be observed. Images of the resulting interface are acquired and the position is measured. The position of the interface is simply related to the viscosity and the flow rate ratio between the sample and the reference. Using dedicated algorithms, sample viscosity is automatically extracted over a controlled range of shear rates and temperatures.

Because of the highly confined conditions, high shear rates can be reached with sample volumes at milliliter range. In addition, constant comparison to a reference solution and working at flow render the measurement calibration free and fully automatic (no need to resample between repetition, automated shear rate and temperature screening). Image based acquisition gives to the user possibility to directly supervise the quality and thus accessing precise and repeatable (1%) measurements.

Fluidicam was designed as a versatile rheometer able to measure virtually any flowing fluid. Its high accuracy even at low viscosities and high shear is a very good fit for inkjet and sprayable formulations or to mimick end-user conditions for lubricants (mechanics, cutting, wire drawing). Viscosity measurement range is simply adjusted by changing the reference liquid, making also Fluidicam a very suitable technique for much thicker, pasty fluids in cosmetics or food. Flow characterization of costly or rare fluids (pharmaceutical products, blood) is made possible owing to its low volume consumption.

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Application of the Least Square Finite Element Method in the Evaluation of the Rheological Behaviour of the Dilute Polymeric Emulsion in Simple Shear Flow

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Micro-structural changes of a second phase in a polymeric two-phase flow system, which can be interpreted as morphology development [1], do not only affect the mechanical properties of the final products, but also change the overall rheological behavior of the polymeric emulsions [2]. In this research, the effect of the second phase deformation on the viscosity of a dilute polymeric emulsion in creeping flow is studied. For this purpose, a three-dimensional computer code is developed to predict the deformation of the second phase in the creeping flow of dilute emulsions. In this approach, the velocity components of the flow field are calculated using the Galerkin finite element method, and a locally applied least square finite element method is employed to predict the nodal values of the volume fraction [3] and the

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explain the micromechanics of biopolymer microgel suspensions very well. We use this technique to study suspensions of plant cells and extract information such as the particle size distribution (PSD) and modulus (G_p) from GDR. Our suspensions are made by suspending potato flakes in water and subsequently sieving them to obtain different size fractions of cells. Gap-dependent and bulk rheology measurements are performed using a parallel plate on a controlled stress rheometer, utilizing necessary adjustments for gap errors that arise with this geometry. A novel routine is performed that includes a compression-relaxation sequence as

the gap is decreased, with small amplitude oscillatory shear performed during the relaxation stage to obtain storage and loss modulus (G', G") as a function of gap. We analyse the measurements using sphere-on-flat Hertzian-elastic-plastic contact mechanics in combination with a particle population model. The model is fitted to the experimental data with particle modulus (G_p) and particle size distribution as fit parameters.

Through this work we demonstrate that this experimental methodology may be used to provide useful insights into the micromechanics of potato cells and can be potentially used to study other suspensions with less-well defined dispersed phase characteristics. This method is applicable to a variety of complex soft particle suspensions from foods and pharmaceuticals to animal and plant cells.

14:20 Marselisborg & Rosenborg Wednesday

Dissolution of concentrated surfactant solutions by time lapse microscopy

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Most of the surfactants used in products for fabrics and home care, such as detergents, have a complex microstructure and rheological behavior [1]. Industrial processing/usage of surfactant-based materials typically include a water dissolution step [2]. It is well established that both physico-chemical and rheological parameters, such as raw material chemistry, type of solvent, temperature and flow conditions, play a key role in the dissolution process. However, the mechanisms governing the dissolution process are not well understood [3]. This study is aimed at investigating dissolution of a viscoelastic surfactant paste in water by advanced microscopy techniques based on Time Lapse observation and automated mosaic scanning. 2D paste disks were confined by 2 circular glass slides, at a given distance. By imaging

advection of the interface, consequently. The volume fraction parameter determines the position of the interface as well as its curvature and normal direction. Therefore, a precise evaluation of the mentioned parameter is vital for a better prediction of the second phase deformation. In order to achieve this target, a new criterion for the interface thickness and a new method for evaluating the second derivative of the volume fraction are suggested. Our results, are comparable with available data in the literature [4], and can predict droplet steady shape as well as its breakup. Using this method, it is shown that the deformation of the droplets and their breakup are parameters which alter the viscosity of the polymeric emulsion. Therefore, the viscosity of a dilute polymeric suspension can be considered as a function of the parameters which affect the second phase deformation, such as deformation rate, surface tension and second phase size.

REFERENCE: [1] Fard, A. S., Famili, N. M., and Anderson, P. D, Comput. Chem. Eng., 32, 1471-1481 (2008) [2] Manas-Zloczower, Ica., 2nd edition, (2009) [3] Mostafaiyan M, Wiessner S, Heinrich G, PPS32, Lyon [4] Sibillo, V., et al., Phys. Rev. Lett., 2006. 97(5)

Wednesday 14:20 Marselisborg & Rosenborg

Pressure drop in microfluidic reactor

Vera Penkavova, Magdalena Bendova, Petr Stavarek, Stanislav Hejda, Hana Vychodilova, Dalibor Vlcek, and Petr Kluson Institute of Chemical Process Fundamentals of the CAS, v.v.i, Prague 16502, Czech Republic

Microfluidic reactors can be advantageously used for specific reactions. In this study the Labtrix START (Chemtrix) platform with a glass microfluidic reactor 3222 was tested from hydrodynamic point of view for planned stereoselective hydrogenation. The hydrogenation will be enabled by a stereoselective catalyst, Ruthenium BINAP complex in mixture of reactants, methanol and water. A presence of ionic liquid (quarternary ammonium salts) allows for an easy separation of this catalyst via its pseudo-immobilisation. The testing of the microfluidic reactor lied in inquiring of pressure drop (PD) during passing through of the reaction mixture. The measurements were performed with mixture of ionic liquid, methanol and water. The PD in the microfluidic reactor of non-trivial geometry is unpredictable via Hagen-Poiseuille equation, because of the PD is increased due to flow separation and recirculations caused by curvature of reactor. The PD should be predicted in terms of an empirical correction of Hagen-Poiseuille equation on the curvature. Firstly, the measurement in a straight capillary was performed with the aim to verify the correctness of the PD measurements (including of subtraction of PD due to surrounding flow infrastructure). Very good agreement between the measured and predicted PD was found in the case of straight capillary. Secondly, the measurement of PD in the microfluidic reactor was performed, followed by PD prediction. Two different approximations of reactor cross-section were used for PD calculation: (i) Hagen-Poiseuille equation included the classical hydraulic radius and (ii) the analytic solution for elliptical cross-section. Both approximations gave very close results. The comparison of the measured and predicted PD in the microfluidic reactor 3222 indicates a correction factor about 2, i.e. the measured PD is about two times higher than the predicted one. Acknowledgements: The financial support by Czech Science Foundation GACR through contract No. 15-04790S is gratefully acknowledged.

Wednesday 14:20 Marselisborg & Rosenborg

Gap dependant rheology as a tool for measuring mechanics of plant cells Omkar S. Deshmukh, Heather M. Shewan, Mauricio Rincon Bonilla, and Jason R. Stokes

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The dynamics of dispersed systems under confinement is anticipated to be a function of the sample's micromechanics. Gap-dependent rheology(GDR) on particle suspensions has previously shown that a reduction in gap causes an increase in elastic and viscous moduli (G',G''), normal force (F_n) and viscosity (η) . We have previously developed a rheological-based 'multi-scale' technique to measure and utilize a population based particle contact model to quantify the dynamics of complex materials in narrow gaps. This technique was found to

the system in bright field or polarized light microscopy as water penetrates the surfactant paste, the dynamic transition among different microstructures was followed. The results were related to the phase diagram and the rheological behavior of the system at different water concentrations. The effect of flow on the dissolution process was also investigated.

[1] H. Li et al., Colloids and Surfaces, 2016. [2] Y. Liu et al., J. of Dispersion Science and Tech., 2015. [3] N. A. Peppas et al., Macromolecules, 1994.

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Ultrafast deformation of colloid monolayers at fluid interfaces: experiments and simulations Marco De Corato, Axel Huerre, and Valeria Garbin

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Droplets and bubbles stabilised by a monolayer of colloidal particles are central in catalysis, encapsulation, and drug delivery. Despite their importance in applications, our fundamental understanding of the behaviour of particle-laden interfaces under dynamic deformation is still limited. While shear deformation has been the focus of recent research, the effect of compression, a leading-order mode of deformation of fluid interfaces, remains largely unexplored, especially at large strain rates. In our work we perform particle-based numerical simulations of spherical colloids adsorbed on a spherical fluid-fluid interface undergoing small amplitude compression and expansion at large strain rate $(10^3 - 10^4 \text{ s}^{-1})$. By modelling the effects of the ultrafast deformation of the interface as effective forces between the particles, and solving for the particle configuration, we predict its microstructural evolution which we characterize in terms of order parameters and pair correlation functions. We find that the periodic compression and expansion of the interface is responsible for a qualitatively different dynamical evolution of the interface. In particular, we observe self-assembly of the particles into a network of strings. The numerical results are compared to experiments in which particle-coated microbubbles are driven into small amplitude compression-expansion by ultrasound forcing at 50 kHz. The peculiar microstructural evolution of the monolayer observed in the experiments closely matches that obtained from our numerical simulations. This work lays the foundations for future studies of high-frequency interfacial rheology of polymer and protein monolayers, with relevance to industrial processing flows.

Wednesday 14:20 Marselisborg & Rosenborg

Structural, microrheological and kinetic properties of a ternary Silica-Pluronic F127-Starch thermosensitive system

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Thermosensitive systems find broad applications in many industrial processes therefore understanding and controlling the stability and microstructure of these systems is of high relevance. In this study, we have used classical rotational rheology and two microrheology methods namely the Multiple Particle Tracking (MPT) and Diffusing Wave Spectroscopy (DWS) techniques to get new insight into structural and dynamical properties accompanying the sol-gel transition of a ternary Silica-Pluronic F127-Starch thermosensitive system. First, we have shown very good agreement in the determination of the sol-gel transition temperature (T_{sol-gel}) between rheological and DWS measurements, latter transition temperature being independent of the sample composition with a constant value equal to ~25°C. Additionally, the kinetics of gelation has been characterized using DWS for the first time and for all samples investigated this transition is very fast, less than 2 minutes. Besides this fast process, a second slow process is observed in the gel state indicating a permanent motion and rearrangement of the structure at longer times. MPT experiments performed in the liquid state show that tracer particles, independently of their diameter, have a purely diffusive behaviour indicating that the micro-environment surrounding the particles responds like a viscous liquid. In the gel state, the variation of the probe size reveals that the size of these areas decreases slowly with time with a characteristic length scale or mesh size less than 1 μ m. Finally, systems with various starch concentration exhibit similar bulk viscoelastic properties in the gel state but different microrheological behavior. This discrepancy is explained in terms of microstructural differences supported by light microscope images.

Wednesday 14:20 Marselisborg & Rosenborg

Reusable Biobased Fracturing Fluid with Low Friction Pressure

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Strict regulatory is now required for storage, handling, and low environmental impact for the fracturing fluid in Sulige gasfield. Therefore, it is desirable to reuse of the flowback fracturing fluid without discharging to environment. This paper reports a new biobased fracturing fluid with low friction pressure. The new biobased fracturing fluid has high temperature stability up to 135 ?C, and fracturing fluid can be broken quickly with low residue. The fluid has low friction pressure and reusable. The new fracturing fluid was field tested in Sulige gas field from 2014 to 2015. The results showed that excellent proppant suspension ability and shear stability. The friction of the fracturing fluid was reduced up to 55% compared with water. The new fracturing fluid has 87% lower friction than that of guar fluid. The amount of proppant in reused fracturing fluid with flowback water can be used up to 530 kg/m3. Average production rate for 33 wells treated with new fluid was 8.46 x 104 m3/day. The total fluid used was 13933 m3 while the reused fluid was 5067 m3. The reuse rate reached to 98%. The reusable cycle of fluid can be up to six wells. The reused fluid has good proppant suspension and stable pumping pressure. Hence, the new reused fluid provides an environmental friendly fracturing operation in Sulige gas field.

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Epoxy resins mixed with ionic liquids and conductive nanoparticles: Interactions and curing kinetics

Mercedes Fernández, Eneritz Garro, Eider Matxinandarena, and Anton Santamaria

14:20 Marselisborg & Rosenborg

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Ionic liquids (ILs) show unique properties such as high ionic conductivity, strong polarity, chemical and thermal stability, excellent solvent properties, as well as low toxicity. ILs are generally considered Newtonian fluids and just a few works report shear-dependant behaviour. On the other side, epoxy resins give rise to polymer thermosets with good thermo-mechanical properties, especially apt for many industrial applications. But, the curing or crosslinking process to harden epoxy resins requires chemical agents, such as amines, that are volatile and toxic. In recent years the use of ionic liquids in the elaboration of epoxy thermosets has deserved a considerable attention in the literature (1). It is claimed that ionic liquids offer a new route to design epoxy networks based on their capacity to facilitate the curing process. Reduction of the curing temperature and time, as well as decrease of amine hardeners concentration, contributes to a sustainable chemistry. Another interesting feature of ionic liquids, linked to the efforts of improving the properties of epoxy resins, is their capacity to disperse properly nanoparticles. In this communication we investigate the rheology involved in the elaboration of nanocomposites based on: a) Epoxy resin and its hardener b) Anionic and cationic ionic liquids c) Multiwalled cabon nanotubes (MWCNT) and graphene platlets (GNP). The viscoelastic behaviour in the linear regime is studied by means of small amplitude oscillatory shear flow (LAOS) and continuous flow are applied to analyse the non linear regime. The research is focused on the searching for rheological evidences of interactions between ILs and epoxy resin and on the viscoelastic analysis of the curing kinetics of pure epoxy resin, epoxy/IL/MWCNT-GNP nanocomposites.

(1) Thi Khan Ly Nguyen et al. ACS Sustainable Chem. Eng. 2016, 4, 481

Wednesday 14:20 Marselisborg & Rosenborg **Screen printing and effect of surfactant on silver particles in paste** <u>NORIYUKI SAKAI¹</u>, Takatsune NARUMI¹, and Ryutaro TAKAHASHI² ¹*NIIGATA UNIVERSTIY, Niigata, Japan;* ²*Namics Corporation, Niigata, Japan*

The front side metallization of solar cells is usually formed by screen printing in manufacturing process of mass production. The fine line printing with high aspect ratio of line shapes is important. The direct observation of screen printing is impossible with current equipment. We subdivided the screen printing processes and observed three steps Filling to the apertures of screen mask, Paste transferring on substrates and substrate snapping-off and Leveling which greatly impact printing shapes to clarify the mechanism of electrode formation. We also created "pseudo-printing simulation equipment" and directly observed the transferring and snapping-off steps in the modeling condition. Four types of silver particle were prepared with the following surfactants: saturated fatty acid coated **A**, unsaturated fatty acid coated **B**, heterocyclic aromatic compound coated **C**, and for reference, uncoated silver **D**.

The four pastes were screen printed on Si wafer used the screen of 30 µm width. Paste C showed the highest aspect ratio and the lowest standard deviation. All pastes showed the same shear viscosity at the shear rate in the filling step. The shear viscosity results did not correlate with filling results. "Pseudo-printing simulation equipment" was assembled to simulate the transferring and snapping-off steps to observe the small releasing hole. The surfactant A and B have the hydrophilic and hydrophobic groups. It causes the top of the electrode to roughen. The surfactant C and D do not include the hydrophilic or hydrophobic groups. It causes the top of electrode to be smooth. Pastes B and C showed higher viscosity in shear rate of the leveling step. It causes narrower width and high aspect ratio. Pastes A and D showed lower viscosity between shear rate. It causes wider width and low aspect ratio.

Wednesday 14:20 Marselisborg & Rosenborg

Flowability of milk powders: influence of processing and fat content and type

Saskia de Jong and Thom Huppertz

Wednesday

Texture & Flavour, NIZO for better food and Health, Ede 6718 ZB, The Netherlands

Milk powders are widely used as ingredient in dairy and non-dairy foods, but also as a consumer product. Besides nutritional and functional properties, powder handling properties are very important to ensure both efficient production and packaging operations, blending of milk powders with other ingredients, but also user experience by the consumer. Flowability of powders is a key parameter in powder handling properties, but full mechanistic understanding of the flowability of milk powder remains to be elucidated. In this study, we evaluated the effect of particle size, particle shape and surface composition on the flowability of milk powders. For this purpose, a series of fat-filled milk powders was used, which differed in the type, and hence melting point, of the fat used as well as the fat content. Furthermore, differences in processing resulted in differences in powder particle size, whereas deviations in particle shape could be studied by comparing spray-dried, agglomerated and roller-dried fat-filled milk powders. Flowability of milk powders was influenced by the size and polydispersity of the size distribution of the powder particles, as well as the shape of the particles. In addition, powder flow was also strongly determined by the properties of the powder particle surface, which was governed primarily by fat and carbohydrates. Carbohydrate contributions were found to contribute in areas where the carbohydrates were in the sticky phase due to exceeding the glass transition temperature. The contribution of fat was found to be related to both the amount of surface fat on the powder particles as well as the crystallinity of the surface fat, which was governed by the melting temperature of the fat. The insights gained from these studies provide mechanistic understanding of factors determining flowability, and hence user experience, of milk powder and also provide practically applicable directions for optimizing this.

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Wednesday 14:20 Marselisborg & Rosenborg Particle interactions and rheology of high-protein bars

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The demand for high-protein bars has grown significantly in recent years. The storage stability of protein bars may be significantly impacted by undesirable textural changes (hardening). The mechanisms responsible for hardening have yet to be fully elucidated but are thought to relate to redistribution of moisture in such non-equilibrium systems. The purpose of this study was to explore the relationships between moisture migration, particle packing, liquid-solid transitions and ageing in protein bar matrices. The textural stability of a whey protein isolate (WPI) powder was compared with that of three whey protein hydrolysate powders. The onset of solidity, defined by the frequency-dependent crossover of viscous and elastic moduli, was dependent on volume fraction and particle interaction energy. Hydrolysis of whey proteins resulted in less extensive hardening. The liquid-solid transition was observed at a volume fraction of 0.73 for WPI and ca. 0.55 for two of the hydrolysates. The most extensively hydrolysed powder did not exhibit an equivalent transition. WPI powder yielded stronger viscoelastic solids at equivalent volume fractions. The rheological properties of bars made using moderately hydrolysed protein powders were consistent with those of weakly, aggregated colloidal gels. Hardening was less extensive in systems in which the liquid-solid transition occurred at lower volume fractions. The relationships observed between viscoelastic behaviour and hardening, were supported by particle size analysis, glass-transition measurements, surface energy analysis and scanning electron microscopy. Rheological characterisation of the liquid-solid boundary, as a function of particle interaction, provides a means by which structural development in concentrated food matrices can be better understood.

Wednesday 14:20 Marselisborg & Rosenborg

Powder rheological analyses of fumed silica

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Powder can be found in almost any industry, where it is manufactured as raw material, intermediate and final product. Thus, knowledge of the powder behavior during a manufacturing process is of major interest. In order to improve the flow behavior of powders, fumed silica is often added because it reduces the bonding forces between the powder particles and thus, flowability is increased. In this study, the rheological behavior of fumed silica was analyzed by using a powder rheometer. The rheometer was equipped with a porous glass frit at the bottom of the measuring cell allowing defined fluidization of the sample. A 2-blade stirrer and a profiled cylinder were used as measuring systems. Cohesion strength, deaeration behavior and apparent viscosity were determined. The fumed silica samples showed low cohesion strength values accompanied by long deaeration times. The results of apparent viscosity showed almost Newtonian behavior at low shear rates, which was independent of the state of fluidization. At high shear rates and full fluidization a shear-thickening behavior was observed whereas low fluidization led to shear-thinning behavior. D43IA007EN-A 3 www.anton-paar.com The obtained results showed that a comprehensive characterization of fumed silica is possible with the used powder rheometer. Furthermore, the findings allow predicting the flow behavior of fumed silica during e.g. fluidized bed processes and pneumatic transport as a powder as well as when it is being used as an additive.

Wednesday 14:20 Marselisborg & Rosenborg

Experimental evaluation of compaction load and duration effects on flowability of thermoplastic rubber (TPR) granular systems

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It is well known that bins or silos filled with granular systems might often show severe problems with discharge of powders or granules, especially when long storage times are considered. These problems are related with (very) long time needed for flow inception and slow discharge, rat-hole and funnel flow or, in some cases, even with no flow at all. When working with industrial systems a number of important variables are to be considered. Such variables may include Particle Size Distribution (PSD), bin and outlet diameter/granule size ratios, presence of inserts close to the outlet, use of anticaking/flow improvers. For our granular systems, some widely used set-ups for flowability testing like wedges and conical hoppers gave us results uncorrelated with the information retrieved from large-scale experiences. Other testing systems like Jenike or Schulze shear cell were instead not available at our labs. In this work, two very simple experimental setups were adopted for studying the effect of compaction load and duration on the flowability of different granular systems of industrial interest. The first set-up was used to evaluate the caking tendency of the granular systems by measuring the normal force needed to crush a granular "cake" and is based on a parallel plate configuration mounted on a MCR301 rheometer. Such system needs a very limited amount of material and can be used for quick and quite reproducible testing of caking tendency. The second set-up is a lab-scale glass bin with square cross-section and a round-hole outlet at the bottom. On top of the granular system it is possible to apply a constant load by means of a chosen weight. The time needed for flow inception, as well as the total time needed for complete discharge after opening the bottom outlet, have been measured during a number of tests at varying applied compaction load and duration. The results obtained instead at lab scale with the two above-mentioned setups were well correlated with those observed at larger, industrial scale.

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Wednesday 14:20 Marselisborg & Rosenborg

The effect of collagen type and concentration on sol-gel phase transition in chitosan scaffolds

Piotr Owczarz¹, Martyna Modlinska², Anna Ryl³, Zofia Modrzejewska⁴, and Marek Dziubinski⁵

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Polymer materials are widely used in medicine as intelligent drug carriers, scaffolds in the processes of cell proliferation and dressings in the treatment of hard-to-heal wounds. Scientists' interest is focused on polymers of natural origin which are mostly biocompatible, biodegradable and non-toxic. Among such polymers there is chitosan, a polysaccharide obtained by partial deacetylation of chitin. It is well dissolved in acid solutions due to protonation of an amino group. Chitosan, as a result of a phase transition induced by an increase in pH or temperature, forms spatial structures linked by hydrogen bonds. A disadvantage of such gels is their small mechanical strength. Since chitosan shows sorption properties for collagen proteins it can form conglomerates with higher mechanical strength. Particularly interesting seems to be the production of chitosan-collagen fibers used in the spinning of dressing fabric. In fiber forming processes an important role is played by rheological properties and temperatures of phase transition of a polymer in the liquid phase. The paper presents results of comprehensive rheological tests for composite chitosan solutions containing various concentrations of two different types of collagen (fish and beef). It was found that at low temperatures (about 5°C), with an increasing collagen concentration the properties of chitosan salt solutions changed from viscous to elastoviscous. At the same time the addition of collagen resulted in lowering the temperature of sol-gel transition and increasing the rate of formation of a spatial gel structure. It was observed that fish collagen with a simpler chemical structure had a much smaller influence on the change of solution properties and decrease of gelation temperature. The shapes of cumulative energy curves obtained at different temperatures and for various types of collagen, showed significant differences in intermolecular interactions.

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PO154 Sol-gel transition of HPC solutions revealed by rheological and Small Angle Light Scattering (Rheo-SALS) measuements

Jerzy Pela, Marek Dziubinski, Piotr Owczarz, and Patryk Ziółkowski

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Hydroxypropyl cellulose (HPC) is a polymer that has been widely used mainly in medical field, ranging from production of artificial tears to controlled drug delivery and also as a dispersion stabilizer in food and cosmetics industries. These applications are possible due to HPCs various rheological properties. One of these attributes is the ability to form an internal structure as a gel. Structure formation occurs in the sol-gel transition, process which in case of the HPC solutions can be controlled by pH and temperature. Missing part of the knowledge of gelation process are parameters and kinetics of the transition.

This paper present results of experimental study conducted in order to describe the mechanism of HPC sol-gel transition which occurs in HPC solutions. Investigation was carried out utilizing highly specific method of Small Angle Light Scattering (SALS) coupled with conventional rotational rheometer. This setup allows SALS investigations simultaneously to all classical rheological tests. SALS is presently developing method of examining internal structures of media. Structure sizes which are possible to examine by SALS are described in the magnitude of micrometers.

Paper presents results of rheological analysis of different concentrations of HPC solutions conducted in order to determine the kinetics of sol-gel transition. Results of simultaneous SALS analysis of the media is presented as well. Rheological measurements were carried out at constant temperature and for conditions of constant temperature ramp from 0,001K/s to 0,1K/s. Preliminary experimental results showed that sol-gel transition is possible to achieve between 25°C to 37°C depending on other process conditions. Such mechanism was confirmed by significant change of viscosity of a sample and changes in light scattering pattern achieved by SALS method.

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Marselisborg & Rosenborg Wednesday 14:20

Understanding and modelling of the viscoelastic properties of slide-ring gels

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Polymer gels and networks are fascinating versatile soft materials that are ubiquitous, from our daily life (foodstuffs, cosmetics, e.g.) to high-tech applications (tissue engineering, sensors, drug delivery e.g.). Among these systems, a very peculiar kind of networks has recently emerged, called "slide-ring gels". Their main crosslinking process is due to topological bonds made of two macrocycles linked together in a figure-of-eight shape, each with a polymer chain threaded into its cavity. These cross-links are not fixed and can slide along the polymer chains of the network and equalize the tension of polymer chains in a manner similar to pulleys; this is called the pulley effect. The complete unthreading of the chain being prevented by bulky groups attached to its extremities. Thus, these junctions are neither covalent cross-links as in chemical networks, nor attractive interactions as in physical networks but are topologically interlocked by movable crosslinks, giving rise to unique properties such as high swelling capacity, extreme softness, ability to equalize internal tensions and huge extensibility while preserving very good shape memory properties. Today, these materials are drawing increasing interest due to their exceptional properties and are promising candidates for several applications such as scratch proof coatings, vibration dampers, or actuators. However, due to these non-usual properties, the dynamics of the slide-ring networks is rather complex and still needs to be understood

based on developing a new tube-based model, in order to fully exploit and control their potential, towards the design of new, smart materials.

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Influence of the viscoelastic regime onto the UV reactivity of PDMS

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Polydimethylsiloxane (PDMS) is a mineral-organic polymer (a structure containing carbon and silicon) with many specific properties. Depending on the size of monomers chain, the non-cross-linked PDMS may be almost liquid or semi-solid. It is a popular candidate in fundamental research and applied sciences to several branches of modern industry. It is used in a wide range of industrial applications (manufacturing textiles, paper, leather goods), in consumer applications (personal-, household-, automotive care products) and in last decades biomedical applications as well.

In our studies, we used an unique method of photo- rheology⁽¹⁾, which allows the simultaneous control physical changes (viscoelastic) during in-situ UV irradiation. We performed our experiments using oscillatory mode at 40 $^{\circ}$ C. At this temperature, the PDMS is in rubbery state. Moreover thermal decomposition of hydroperoxides is limited.

We performed two kind of experiments; monofrequency and multifrequency, without and with UV irradiation. Our results showed that depending on the frequency used, the PDMS behaves like Newtonian or non-Newtionan fluid. Below 6.5 rad s^{-1} , both Eta' and Eta" increase (crosslinking reactions) and above this point we observe decreasing of them (like for degradation reactions). This limit 6.5 rad s^{-1} seems to correspond to the cross over point of Eta' and Eta" in frequency test. The application of UV irradiation led to an increase of this effect.

[1] Photochemical reactivity of PLA at the vicinity of glass transition temperature. The photo-rheology method. A. A. Marek, V. Verney, *European Polymer Journal*, 2016, **81**, 239-246.

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Wednesday 14:20 Marselisborg & Rosenborg

Viscoelastic properties of 3D-printed materials, comparative study with injection moulding

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Fused deposition modeling (FDM) is one of the most widely used technologies in rapid prototyping suited for producing parts with complex geometries. On the principle of layered manufacturing, the melted polymer filament is extruded through a heated nozzle and formed. Polylactic Acid (PLA) is one of the most commonly used 3D printing filaments. Generally, PLA is made into useful items using thermal processes like injection moulding and extrusion. Therefore, its rheological properties, especially its shear viscosity, have important effects on thermal processes. Meanwhile, PLA has low thermal stability, which limits their large scale applications. The purpose of this work is to investigate the thermal degradation of PLA, upon injection moulding and fused deposition modeling processes and to optimize the manufacturing parameters for FDM (temperature, raster angle, printing order...), in order to improve the mechanical properties.

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Effect of uniaxial and planar extensional viscosities, die exit stress state and Deborah number on neck-in phenomenon during extrusion film casting

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In this work, viscoelastic, isothermal extrusion film casting modeling utilizing 1D membrane model and modified Leonov model was performed in order to understand the role of uniaxial and planar extensional viscosities, viscoelastic stress state at the die exit and Deborah number on the polymer melt film stretching in the post die area. Experimental data for LDPE and theoretical predictions based on the eXtended Pom-Pom (XPP) model taken from the open literature were used for the validation purposes. Acknowledgments: The authors wish to acknowledge Grant Agency of the Czech Republic (Grant registration No. 16-05886S) for the financial support.

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Elastic instabilities in planar elongational flow of monodisperse polymer solutions

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We use a combination of full-field birefringence imaging and time-resolved flow velocimetry to examine the onset of elastic instabilities in viscoelastic polymer solutions flowing at low Reynolds numbers (*Re*) through a cross-slot-type microfluidic device. We employ well-characterized, nearly monodisperse polymer samples and an optimized cross-slot geometry that generates a close approximation to ideal planar elongation with hyperbolic streamlines. As we increment the Weissenberg number (*Wi*) through manipulation of the macroscopic flow rate, our results reveal the onset of a new mode of elastic instability for $Wi > Wi_{c1}$, which is characterized by lateral displacement and spatiotemporal fluctuation of the stagnation point along the outflowing symmetry axis. A second large scale symmetry breaking instability

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occurs for a higher critical Weissenberg number Wi_{c2} , which is also unsteady and resembles previously reported purely elastic flow asymmetries. We map the progression of instabilities in Wi-Re parameter space for fluids of different elasticity number, El = Wi/Re. In addition, near the onset conditions of the first instability at $W_{i_{c1}}$, we are able to evaluate a well-known dimensionless criterion that predicts the onset of elastic instabilities based on rheological and geometric scaling parameters. We find good correspondence between values of the criterion previously reported for flows dominated by shearing kinematics and those obtained in our planar elongational flow field. This result strongly suggests that the onset of elastic flow instabilities in this elongational flow field is driven by the accumulation of elastic tensile stress along strongly curved streamlines that pass close to the stagnation point.

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Viscoelastic shear flow through wavy-wall microchannels Simon J. Haward and Amy Q. Shen

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We examine the flow of viscoelastic polymer solutions through glass microchannels with one planar and one wavy wall bounding the channel width. The channels are fabricated with high depth (d) to width (w) ratios and with small wave amplitudes $A \ll w$. Polymer solutions with a range of rheological properties (specifically elasticity numbers El and viscosity ratios β) are formulated by dissolving high molecular weight polyethylene oxide (PEO) into aqueous solvents viscosified using low molecular weight polyethylene glycol (PEG). Wavy wall microchannels are fabricated in fused silica by selective laser-induced etching. Channels are tested with various dimensionless widths 0.6 < a = 2pw/? < 10, where ? is the wavelength of the wavy surface. We employ micro-particle image velocimetry (μ -PIV) to measure the flow field within the microchannels as we increment the imposed Weissenberg (Wi) and Reynolds (Re) numbers for various fluids. In all cases we observe vortical perturbations being generated close to the wavy surface with positive vorticity rolls above peaks and negative vorticity rolls above troughs. However, there is a subtle interplay between the rheological properties of the fluids, the magnitude of a, and the imposed flow conditions that affect the shape of the vortical rolls and the distance from the wall at which the maximum vorticity occurs (defined as the "penetration depth"). We confirm the existence of three broad flow regimes, described as "shallow-elastic", "deepelastic" and "transcritical" [1] that can be effectively summarized in a phase diagram in an appropriately defined dimensionless parameter space.

[1] J Page & TA Zaki, Viscoelastic shear flow over a wavy surface, J. Fluid Mech. 801: 392 (2016).

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Wormlike micelles instabilities : rheology fundamentals

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Polymer solutions have many applications in the industry. Their main issue is the irreversible breakage of the polymer chains under high shear rate. One alternative to avoid this problem is to use giant micelles, also called wormlike micelles (WLMs). These micelles increase the viscosity of solutions, and giant micelle solutions have a shear thinning behavior similarly to polymer solutions. WLMs can be considered as living polymers as they result from the self-assembly of surfactant molecules with dynamic breakage and micelle reformation occurring continuously.

The surfactants used in this rheological study are long chain Alkyl amidopropyl betaines. At a fixed volume fraction, the response of the solution depends on shear rate, temperature, and initial state. Under controlled conditions, the viscosity increases and decreases with temperature in varying temperature ranges depending on shear rate. Even though Micelle length and relaxation time decrease with temperature, those apparent viscosity increases are still observed; a possible reason for this behavior could be an effect of elastic instabilities. The establishment and control of these instabilities are not well understood. Numerous works have been done on WLM instabilities. Most of them dealt with the occurrence of shear banding within the shear stress plateau (stress is constant over a range of shear rate). Our system despite having such a plateau does not display shear banding.

In this work, we first try to study the fundamentals of this fluid which are not as simple as one might expect. For instance, its response to a simple shear flow is not yet understood as the solution relaxes while it is flowing. Moreover, its response for a constant shear rate also varies with the initial state i.e. resting time or shear history. We also observed some variations of shear stress around a mean value which are dependent on temperature for a fixed shear rate. These variations have the same evolution with temperature as the viscosity.

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Micro-Heterogeneity and Micro-Rheological Properties of High-Viscosity Barley B-Glucan Solutions Studied by Diffusing Wave Spectroscopy (DWS)

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Soluble fiber ß-glucan is one of the key dietary materials in healthy food products known for reducing serum cholesterol levels. The microstructural heterogeneity and micro-rheology of high-viscosity barley ß-glucan solutions were investigated by the diffusing wave spectroscopy (DWS) technology. By comparing the mean-square displacement (MSD) of the microspheres imbedded in eight concentrations of β -glucan solutions, we found that the solutions exhibited nearly homogeneous behavior at =0.1 %, but the material showed a clear degree of heterogeneity at =0.25 %. Micro-rheology investigation revealed that ß-glucan solutions displayed nearly perfect viscous behavior at =0.1 %, but the property changed into viscoelastic one at =0.25 %. The magnitude of high-frequency viscoelastic moduli for the 0.25 % - 0.75 % ß-glucan solutions can be characterized by G*?? ?^3/4, which is the semi-flexible polymer behavior.

However, the magnitude of high-frequency viscoelastic moduli (G^*) for the 1.0 % - 1.25 % ß-glucan solutions is proportional to ?^1/2, which is the flexible polymer behavior. All micro-structural heterogeneity and microrheological property shifts occurred in relatively small concentration ranges.

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Newtonian and viscoelastic flow dynamics around 2D microbot prototypes

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The use of microbots constitutes nowadays a minimally invasive procedure in biomedicine. It causes widely patient-oriented benefits as reduction of recovery time, medical complications, infection risks, and postoperative pain to increase quality of care, including preventative care [1]. Manipulation and applicability of these microdevices are challenging tasks and some technical issues must be solved in order to standardize their use in clinical protocols. This work aims to optimize the dynamic efficiency of microbots in similarity complex fluid flows to human blood flow, to that end different approaches in 2D and 3D were considered. However, at the micro-scale, due to the elastic effects are enhance, the assumption of the validation of studies of flows around different prototypes in 3D with a 2D approach is very critical. Martínez-Aranda et al. [2] studied the influence of the microbot prototype morphology in the velocity field of Newtonian and viscoelastic fluid flow of Newtonian and viscoelastic fluids around 2D microbot prototypes. Polydimethylsiloxane (PDMS) microchannels were fabricated with different 2D prototypes. The 2D microbots consisted in pillars with the same cross sections of the 3D microbots in [2], i.e. a cylinder as 2D analogue for a sphere in 3D, a prism with square base for a cube, and prims of elliptic bases for ellipsoids. Results allowed the comparison with the 3D study performed by [2] and showed that the ellipse 1:2 presented higher flow symmetry before and after the model, especially for the non-Newtonian blood analogue, as in the 3D study.

[1] Nelson, B. J., et al. (2010). Annu. Rev. Biomed. Eng., 12,55-85.

[2] Martínez-Aranda, S., et al. (2016). Soft Matter, 12,2334-2347.

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Wednesday 14:20 Marselisborg & Rosenborg

Newtonian and non-Newtonian fluid flow simulation in artificially generated porous media

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Flow and transport in porous media are often encountered in chemical, pharmaceutical and food as well as petroleum and groundwater engineering and in many other industrial applications. In this way, to improve the physical understand for such ?ows and the accuracy of existent models, the study of more realistic geometries would be necessary. In the current work we present a strategy to generate a highly complex 3D porous media. The 3D porous media is generated by a controlled random function. Frequency points are controlled by a Fast Fourier Transform (FFT) algorithm, allowing control the region with more pores or fractures. Pore-scale simulations were conducted on 3D porous media using OpenFOAM CFD, for single and two-phase flow for Newtonian fluids and single-phase flow for non-Newtonian fluids. Porosities, permeabilities and pressure drop results have been compared with the literature data. The accuracy and stability of the numerical method have been verified through the development of several test cases. The results showed the potential of the method to predict multiphase ?ow and the viability of the 3D porous media generator to perform CFD simulations of different materials.

Wednesday 14:20 Marselisborg & Rosenborg **Mesoscopic Model with Vectorial Structure Parameter for Star Polymers** <u>Barry W. Fitzgerald¹ and Wim J. Briels²</u>

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The emergence of many rheological properties in complex fluids, such as polymeric systems, can be attributed to the deformation of the particle entities due to sliding motion. Some complex fluids may exhibit a shear thinning response, which is linked to the particle deformation or variation and resulting relaxation of some structural property within the fluid. In previous numerical studies this structural property has been referred to as inter-particle entanglement or interdigitation. We present an updated mesoscopic model to describe the transient forces that develop due to the relaxation of the structural parameter between two star polymers. Transient forces are calculated from the response of a vectorial structure parameter between the star polymers. This calculation approach differs from previous studies where the transient force is estimated from the relaxation of a scalar structure parameter. The use of the vectorial structure parameter reproduces forces from previous small scale simulations while also correcting for an unphysical feature observed in an earlier mesoscopic model.

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Cross-WLF parameters to predict rheological properties of polylactic acid

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Poly(lactic)acid is one of the most important biodegradable polymers developed on a large scale and produced using renewable feedstock and by means of bacterial bio-activity. Predicting its rheological properties starting from the molecular weight distribution has not been possible up to now mainly because thermal degradation processes seriously affected the reliability of many attempts to measure its LVE. In addition ring opening polymerization (ROP) does not allow to span a sufficient range of polydispersity index values to validate molecular models. As a consequence the parameters governing the dynamics of the polymer chains in the melt are not yet available. Only in the last few years, for instance, it was recognized that reptation correctly applies to this biopolymer with the usual power law molecular weight dependence of the viscosity of the entangled melt with the expected exponent 3.4. In this work a series of commercial PLA samples synthesized by ROP and with different Mw has been investigated with the aim to calculate the correct Cross-WLF parameters able to predict the MWD, temperature, pressure and shear rate dependence of the shear viscosity. A simple model based on free volume arguments was also taken into account to predict the viscosity of PLA/lactide concentrated solutions.

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A two-phase solver based on Phase Field method

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In this work we present the performance of a two-phase solver which is based on a diffuse interface approach and is implemented on top of an in-house viscoelastic single-phase solver [1]. The Phase Field method is considered and the Cahn-Hilliard equation [2] is employed for describing the transport of a binary fluid system. The interface between the two fluids adopts a continuum approach, which is responsible for smoothing the inherent discontinuities of sharp interface models, facilitating studies that are related to morphological changes of the interface, such us as droplet breakup and coalescence.

A range of 2D test cases are investigated in order to validate the implementation: the Rayleigh-Taylor instability, the oscillation of a square droplet and the deformation of a droplet under constant shear. For all cases, the two-phase solver manages to predict the expected dynamics presenting an overall good performance. More specifically the solver is able to capture the interfacial patterns of the Rayleigh-Taylor instability for the two Atwood numbers under consideration, At=0.5 and At~1. The expected patterns of the interface instability for the case of At=0.5 are predicted with great accuracy for all dimensionless times. For the case of the oscillating droplet, the local higher levels of curvature of the initial state are translated into a pressure imbalance generating an oscillatory movement. The droplet takes various forms during this oscillatory movement and finally ceases to a static circular drop. At rest, the system predicts the result expected from the Young-Laplace equation. Finally, for the droplet deformation case we are able to predict the corresponding history of the deformation in good accuracy for a range of conditions, e.g. for a capillary number, Ca=0.6 and a Reynolds number Re=0.3.

[1] PJ Oliveira et al, J Non-Newton Fluid Mech, 79:1 (1998). [2] JW Cahn and JE Hilliard, J Chem Phys, 28:258 (1958).

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Surface rheology of block copolymer stabilized interfaces: a combined experimental, theoretical and computational study

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Complex fluid-fluid interfaces can be formed by a wide range of surface active components, such as proteins, colloidal particles, polymers, lipids, or mixtures of these components. In this study, our goal is to characterize the micro-structure and mechanical properties of fluid-fluid interfaces stabilized by multi-block copolymers, using a multiscale multidisciplinary approach, which integrates state of the art computational methods, surface rheological and interfacial structure evaluation experiments and nonequilibrium thermodynamics. Using Monte Carlo (MC) and nonequilibrium molecular dynamics (NEMD) simulations, surface microstructure, surface rheological properties, and the surface free energy in terms of a set of structural variables can be obtained. Using the results from both experiments and computer simulations as a starting point, we will develop nonlinear coarse-grained constitutive models in the GENERIC framework, able to describe the stress response and structural evolution of the interface as a result of an applied deformation. We will determine the mechanical properties and interfacial structure as a function of surface polymer concentration, chemical structure of the polymers (variation of number, size, and distribution of blocks) and degree of hydrophobicity and rigidity of the sub-blocks. In this manuscript, we just focus on equilibrium properties of such systems obtained from MC and MD simulations, including adsorption, surface tension isotherms and the interfacial microstructures.

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Drop coalescence in the presence of elastic interfaces

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The present work is concerned with experimental studies regarding the coalescence of a single liquid drop with the liquid beneath an interface. The experimental metodology is as follows: a liquid drop is formed in the above lighter layer, it falls and reaches the interface. After a resting time, coalescence begins with the forming of an orifice in the interface. The drop's liquid is drained through a capillary bridge/filament in the liquid layer below the interface. Depending on the rheological properties of the liquids involved, the evolution of this capillary bridge/filament influences the coalescence dynamics, like formation of secondary daughter droplets or total time of the merging. In the case of liquid - air interfaces, partial coalescence, formation of smaller daughter droplets, can be observed when the drop is merging. By increasing the viscosity in the above fluid layer, like in the case of liquid - liquid interfaces, this partial coalescence can be supressed. By adding polymers or surfactans, the interface becomes elastic. Photos were acquired with a fast CMOS camera attached to an objective with a microscopic magnification. Differences regarding coalescence evolution were analyzed by comparing drop coalescence with the liquid beneath an interface for different Newtonian liquids and polymer solutions. The effect of rheological properties over the coalescence dynamics is indicated.

Wednesday 14:20 Marselisborg & Rosenborg Measurement of Surface Visco-elasticity by EMS method

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Recently developed disk-type electro- magnetically spinning (EMS) viscometer has been successfully employed also for measurements of mechanical properties of liquid surface, besides the bulk viscoity. For example, two-dimensional viscosity of the mono-molecular films adsorbed on the water surface was measured with the system. In the two-dimensional system, the hard circles freely floating in the media are considered to show contribution to the change in the viscoelastic properties, in which the modeling of the transposition of particles is much easier. In the presentation, we report the measurement of the surface viscosity of the liquid surface containing two-dimensional colloidal particles. The disk-type EMS system could detect the distribution of the surface flow due to the rotation of the probe disk. It can also obtain the excess viscous torque, which is converted to the surface viscosity as a function of the surface concentration of colloidal particles. The sample is the water surface, on which micro carbon particles are dispersed. With these samples, we carried out the measurement of the distribution of the surface flow by observing the motion of the particles. The motion was taken as movies, through which the tangential speed of the particle is obtained. As a result, we can see the rotational speed of the probe rotor and its rotational speed, and determined the surface viscosity as a function of the surface colloidal system. We can see that the surface colloidal system. We can see that the surface viscosity increases with the colloid density and the relation is almost propertional. These macroscopic model of colloidal systems would be helpful for the understanding the rheological properties of the actual 3D colloidal systems.

Wednesday 14:20 Marselisborg & Rosenborg Capillary effects on fluid invasion process

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In primary cementing, pressure imbalance between the formation fluid/gas and the cement slurry (occupying the annular space formed between the steel casing and borehole) causes annular gas migration. Gas migration can have serious impacts on the environment, safety and the well productivity. In the case of a purely viscous fluid, a pressure over-balance is sufficient to ensure that formation fluid enters the annulus. However, the cement slurry is a yield stress suspension and further develops a gel strength during early stage hydration. In this case, we may suspect that the yield stress has a significant difference on resisting fluid invasion. The main difficulty is finding the critical pressure at which fluids begin to invade the well, since the onset of flow relates directly to the unknown position of the yield surfaces, which are mainly a function of the well geometry and the rheology of the slurry. We present results of a systematic study of this problem to distill the important physical parameters. We began with the simplest model, injecting a Newtonian fluid to a column of yield stress fluid, where yield stress and aspect ratio of the column were identified to characterize the invasion process occurs in five stages: mixing, invasion, transition, fingering/fracture and arrest stage. In this first study a miscible iso-dense fluid was injected and the role of surface tension was considered to be negligible. We carried out this research to study the effect of surface tension between the fluids on invasion process. In this study we discuss the results obtained by injecting an immiscible and iso-dense fluid into a yield stress fluid.

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Flow of a ferrofluid in a rectangular driven cavity in the presence of uniform magnetic fields Camila O. Vieira¹, Yuri D. Sobral², and Francisco R. Cunha³

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In this work we studied different flow configurations of ferrofluids in a rectangular cavity, in which the top boundary is moving. A similar study has been carried out in [1] for superparamagnetic fluids in square cavity. We proposed a vorticity-streamfunction formulation to solve the flow, and both the hydrodynamic and the magnetic field equations are solved using a finite differences scheme. We identify the dimensionless physical parameters of the problem as the Revnolds number and the Magnetic Revnolds number. The magnetic field is locally solved instantaneously. We tested various configurations magnetic fields and different constitutive models for the ferrofluid magnetization [2,3,4]. We used this well known geometry to study the effects of the term μ_0 **rot(MxH)** on the flow of ferrofluids, specially under uniform applied magnetic fluids.

References

elastomers

[1] E.E. Tzirtzilakis e M.A. Xenis. Biomagnetic fluid flow in a driven cavity. Meccanica, 48:187-200, 2013.

[2] M.I. Shliomis, Effective viscosity of magnetic suspensions, Soviet Phys JETP, 6:1291-1294, 1972.

[3] M. I. Shliomis. Magnetic Fluids, Soviet Phys Uspekhi, 2:153-169, 1974.

[4] R.E. Rosensweig, Ferrohydrodynamics, Cambridge University Press, 1985.

Wednesday 14:20 Marselisborg & Rosenborg

Rheo-optical investigation of waxy crude oil emulsions in shear flow Sergio Caserta

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Waxy oils are a relevant fraction of non-conventional crude oils, that differ from traditional hydrocarbons for density, viscosity and composition. Wax deposition during multiphase pipeline flow is a common problem in transportation step of upstream processes. Wax molecules in the crude oil mixture can crystallize and solid wax particles can deposit on the pipe wall. The presence of water, present or intentionally added during upstream processes, make the rheological behavior of these fluids even more complex. In particular, wax crystals can accumulate at the oil-water interface, inducing the formation of complex structures. Aim of this work is the morphological characterization of waxy crude oil emulsions during flow. For this purpose, using a well-known procedure, a model fluid has been formulated by mixing mineral oil and paraffin wax. The rheological properties of this model reproduce the typical fluid behavior of raw oils, in a wide temperature range. The study is focused on the deformation and relaxation of water drops in shear flow, analyzed by a parallel plates rheo-optical apparatus. The ultimate goal of this research is the fundamental understanding of the influence of fluid microstructure on several aspects of oil upstream, ranging from flow assurance, to enhanced oil recovery.

Wednesday 14:20 Marselisborg & Rosenborg

The role of sucrose concentration in self-assembly kinetics of HM pectin

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Influence of material composition on properties of silicone matrix materials for magneto-theological

Several biopolymers are widely employed in food, pharmaceutical and biomedical sectors by virtue of their ability to generate supramolecular structures, typically physical hydrogels. In the case of high methoxyl pectins (HMP) the gel formation is promoted by the presence of cosolutes (sugars or polyols) and low pH. The present investigation regards the structuring kinetics of aqueous HMP solutions having different glucose content at 20°C. A sequence of consecutive frequency sweep was applied to each sample immediately after its preparation. The time evolution of the linear viscoelastic behavior is described by the sigmoidal profiles of both moduli at each applied frequency and more thoroughly defined through the change of the mechanical spectrum, i.e. the variation of the parameters of the generalized Maxwell model or the Friedrich-Braun model which are both suitable to provide a satisfactory data fitting.

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Magneto-rheological elastomers are an interesting class of smart materials which change their properties under the stimulus of a magnetic field, due to particle-particle interactions induced by the field applied. However, the performance of such a composite material depends of the properties of the rubbery matrix as well as on the particulate fillers' properties and on the volume fraction of added filler.

Therefore, the paper discusses the influence of stoichiometry on crosslinking kinetics determined by rheology for unfilled platinum catalyzed 2K-RTV silicones. Swelling experiments in toluene are evaluated with respect to the number of crosslinks per volume and to the swelling kinetics for various ratios of resin component A to component B. The maximum crosslinking density was achieved for the stoichiometry recommended by the resin manufacturer of A:B=2:1. Higher or lower contents A:B ratios results in lower crosslink densities and consequently lower moduli. The extract obtained in the swelling experiments contains silicone molecules which are not bound to the network. It is quantitatively analyzed by GPC as a function of resin composition. Component A and B are similar in their mono-modal

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molar mass distribution. However, a clearly bimodal distribution of the polymer molecules extracted from in the network is found. The amounts of high (probably partially cross-linked) and low molar mass components scale with composition.

Finally the influence of temperature on the frequency dependence of the neat matrix and magnetorheological elastomers based on it are analyzed over a wide range to temperatures with respect to frequency-temperature superposition.

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Spectral Laser Freezing Point Depression Osmometers for Medical Biochemical / Biophysical Measurements and Automatic Recording of Physico-Chemical Dynamics and Reaction-Diffusion Kinetics of Biocrystallization Using Tunable Diode Laser Modules and AOF

<u>Theodor Orehov</u>¹, E. Zaytsev², and O. Gradov³

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This report describes a design of a new spectrophysical analytical instrument based on a freezing point depression osmometer, which is capable of dynamic monitoring and automatic recording of physico-chemical dynamics and kinetics in freezing point depression osmometry of biological liquids [1], dairy products [2], ferrofluids [3], fuels and oils [4], etc. Similar techniques may be used not only for "macroscopic" devices, but also for nanoliter osmometer devices and their microminiaturized analogues, such as laser freezing point "osmometer-on-a chip" devices for laser cryobiology studies using tunable laser diodes. We propose a new kind of laser freezing point osmometers based on synchronous, parallel or serial application of parametrically different tunable laser modules with unequal light beam characteristics, such as wavelength and power (in a certain range). The laser freezing point depression osmometer / laser nanoliter osmometer modification for the determination of the melting and freezing points of an aqueous solution is available for the low-cost student-oriented laboratories, as well as for well-equipped industrial labs, since optical waveguide-based spectrometers (which may be used as detectors for different kinds of tunnable diode laser sources) are rather available for routine applications [5]. Laser nanoliter osmometer which allows using of the sample volumes about several nanoliters consists of: a controller box, a cooling stage, a rotating tunable laser source module, an optical waveguide / fiber optic spectrometer module, various micrometer syringes, a stereoscopic trinocular microscope equipped with a cooled CCD camera with different filters for spectrozonal / multispectral registration and a sample holder.

[1] O. V. Gradov, Journ. New Med. Technol., 20(1):123-125 (2013) [2] O.V. Gradov, Dairy Farm. Journ. {ISSN: 2225-4269}, (7):46-56 (2012) [3] O.V. Gradov, F.K. Orekhov, E.V. Zaytsev [DOI: 10.5281/zenodo.14548]. [4] E.V. Zaytsev, Chem. Technol. Fuels & Oils, 51(6):796-798 (2015).

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Shear induced orientation effects in optical active samples characterized with polarized light imaging Loredana M. Völker-Pop, Tobias Nill, <u>Gunther Arnold</u>, and Jörg Läuger

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While the classical rheology gives information about the macroscopical behavior of a material under certain conditions, this behavior is strongly determined by the underlying microstructure of the material itself. Thus, the combination of optical techniques with rheological measurements might be of interest in order to correlate microstructural properties with the rheological behavior of the material. One of these techniques is polarized light imaging which allows e.g. the observation of flow induced crystallization processes of polymers or the characterization of the orientation of polymer chains in polymer solutions and melts under shear [1-3]. The method is based on the phase difference of light passing through optical active materials and provides information on optical path boundaries between optical isotropic and anisotropic structures. The phase differences can be analyzed by an optical setup consisting of light source, collimating lens, polarizer, analyzer and CCD camera. This contribution will present a polarized light imaging setup mounted on a Modular Compact Rheometer (Anton Paar) and highlight applications which indicate the usability of this technique in order to correlate microstructural changes with the rheological behavior of different samples. Different polymer solutions were investigated with cone-and-plate and parallel-plate geometries in order to visualize possible effects of non-constant shear rate on the shear induced orientation within the sample. Additionally the impact of shear on the behavior of liquid crystals was determined at different temperatures in order to evaluate the crystals' transition from the isotropic to the anisotropic state. The results indicate the suitability of the combination of polarized light imaging and rheology to monitor shear induced transformations in complex fluids.

[1] Holland, C. et al. (2012) Adv. Mater. 24, 105-109. [2] Mykhaylyk, O.O. et al. (2012) Macromolecules 45, 5260-5272. [3] Mykhaylyk, O.O. et al. (2016) J. Polym. Sci. Pol. Phys. 54, 2151-2170

Wednesday 14:20 Marselisborg & Rosenborg

Characterization of summer tire tread compounds by Large Amplitude Oscillating Shear (LAOS) <u>Michael Heinz</u>¹, Jochen Kroll², and Thomas Rauschmann³

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In the last years, characterisation of plastics by Large Amplitude Oscillating Shear (LAOS) became a high-power, widely spread technique. Also for elastomers (especially different EPDM types) this method is applied, using a Fourier Transformation (FT). Regarding this background investigations with Fourier transformation rheometer were carried out for the non-linear viscoelastic domains for summer tire tread compounds based on the "green tire recipe", a compound including a silica/silane reinforcing system. In this connection, not only the character of the polymer was changed but also differences in filler and silanes were realised. In particular was determined, who to detect polymer architecture with this tool and whether there is a potential of this approach to select filler behaviour as surface area and/or structure as well as the bounding type of different silanes in a repeatable way.

Wednesday 14:20 Marselisborg & Rosenborg Secondary flows due to finite aspect ratio in inertialess viscoelastic Taylor-Couette flow

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Both in rheometry and in fundamental fluid mechanics studies, the Taylor-Couette geometry is used frequently to investigate viscoelastic fluids. In order to ensure a constant shear rate in the gap between the inner and outer cylinders, such studies are usually restricted to the small-gap limit where the assumption of a linear velocity distribution is well justified. In conjunction with a sufficiently large aspect ratio (i.e. ratio of cylinder depth to gap) the flow is then assumed to be viscometric. Here we demonstrate, using a perturbation technique with the curvature ratio as the perturbation parameter, and full non-linear simulations using a finite volume technique, that even in the creepingflow (inertialess) limit, for viscoelastic fluids end effects due to finite aspect ratio always gives rise to a secondary motion. Using the constant-viscosity Oldroyd-B model we are able to show that this secondary motion, as has been observed in related pressure-driven flows with curvature such as viscoelastic Dean flow, is solely a consequence of first normal-stress differences and curvature. Our results show that the end effects can significantly change the flow characteristics, especially for small aspect ratios, and this may have important consequences in some situations such as the onset criteria for purely-elastic instabilities.

A New approach for simulation viscoelastic flows at high Weissenberg numbers using the hyperbolic

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tangent of conformation tensor Azadeh Jafari, Alireza Chitsaz, and Reza Nouri

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This study presents a new approach so called hyperbolic tangent to preserve both symmetric positive definite of the conformation tensors and also bound the magnitude of eigenvalues. The idea behind this transformation is due to numerical evidence of matrix logarithm formulation originally proposed by Fattal and Kupferman (J. Non-Newtonian Fluid Mech. 123 (2004)). Solving the constitutive equation in the new scale, logarithmically, let the eigenvalues of the new conformation tensor range from infinite positive to infinite negative while reconstructing the classical conformation tensor from either infinite positive eigenvalues or infinite negative eigenvalues does not have any physical meaning. This enhanced formulation, hyperbolic tangent, prevails the previous numerical failure by bounding the magnitude of eigenvalues in a manner that positive definite is always satisfied. On the other hand this new formulation possesses a unique modelling capability and has the potential to provide state-of-the-art numerical simulations of viscoelastic fluids. Numerical simulation of FENE-P model in Poiseuille flows proves that the hyperbolic tangent formulation can achieve higher Weissenberg number comparing the Logarithmic and Classical formulations.

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Simulation of core/annular flow of viscoelastic/Newtonian fluids using spectral element method

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In this Paper, it is intended to simulate the pipe flow of a viscoelastic fluid surrounded by a Newtonian one. The Oldroyd-B model is considered for the viscoelastic fluid and the concentration equation is solved to simulate two phase core annular flow regime in addition to continuity and momentum equations. A solver is developed to model Oldroyd-B flow and another for diffusion equation based upon a spectral element method framework. Analytical solution for Poiseuille pipe flow of Oldroyd-B fluid is presented. The main goal is to assess the frictional pressure gradient of core annular flow along the pipeline to compare with single fluid flow and the effect of rheological properties like Weissenberg number and ratio of viscosities on pressure loss.

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