

Rheology of Polymerically Stabilized Colloidal Suspensions

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ABSTRACT

Stable colloidal suspensions are, physically speaking, relatively simple systems. Yet, they display a wealth of rheological phenomena. Here, systems are considered in which stability is ensured by polymers that are chemically grafted onto the particle surface. The general rheological behaviour and suitable scaling laws for these systems are reviewed.

INTRODUCTION

Adding small, colloidal particles to a Newtonian fluid can alter the rheological behaviour drastically. The non-Newtonian effects become very pronounced at higher particle concentrations. The rheological phenomena have been recently reviewed by Barnes et al.¹, the relation to structure and colloidal parameters by Russel et al.². If the particles have a tendency to aggregate together, adding one volume percent might be enough to change a fluid into a weak solid, displaying elasticity and yield stress. The rheology of flocculated systems is not yet completely understood because of the complexity and the flow-dependency of the microstructure.

For colloidally stable systems, where the individual particles do not stick together, the basic rheological phenomena are well documented now, at least for spherical particles. The viscosity curves and the dynamic moduli will be reviewed here for steric, i.e. polymerically, stabilized dispersions. Model systems of this type can be prepared that contain monodisperse spherical particles. They have been used to investigate the role of the various parameters affecting the rheology.

COLLOIDAL FORCES

In a first step the contributing factors have to be identified. The present discussion is limited to systems containing monodisperse spherical particles. Dimensionless expressions are used for the param-

eters, as originally introduced by Krieger³, in order to generate generally valid relations. In flowing suspensions the hydrodynamic forces are transmitted through the suspending fluid. Hence they are proportional to the viscosity η_m of this fluid. Therefore the viscosity η of the suspension is scaled with η_m , meaning that relative viscosities are used:

$$\eta_r = \eta/\eta_m \quad (1)$$

During flow the hydrodynamic forces will tend to drag the particles along in a convective motion whereas Brownian motion acts towards restoring the equilibrium structure which exists at rest. The ratio between the two forces, or between the corresponding time scales, provides a dimensionless measure for the shear rate. In dilute systems it is given by a Peclet number. For nondilute systems the mobility of a particle is strongly affected by its neighbours and thus by concentration. This is taken into account, following Krieger³, by replacing the medium viscosity by the suspension viscosity at the shear rate under consideration. The result is a reduced or dimensionless shear stress σ_r :

$$\sigma_r = \eta \dot{\gamma} a^3 / kT \quad (2)$$

where a is the particle radius, $\dot{\gamma}$ the shear rate, k the Boltzmann constant and T absolute temperature.

Particle inertia might also interfere. Hence a particle Reynolds number Re_p has to be considered:

$$Re_p = \rho_p \dot{\gamma} a^2 / \eta \quad (3)$$

Lacking systematic information about its effect the Reynolds number is normally ignored, but this might be an oversimplification.

If only hydrodynamic and thermal forces would act on the particles ("Brownian

hard spheres”) the steady state viscosity would be a unique function of σ_r (neglecting Re_p) for a given volume fraction of particles. This function is known from experiments on model systems (de Kruif et al.⁴). Present theoretical predictions can describe the experimental results quite well (Russel⁵).

In most real systems the London-van der Waals forces cause attraction between the particles and thus induce flocculation. Stability can be restored whenever an adequate interparticle repulsion force is generated. In aqueous media electrostatic repulsion can be used effectively. A more general procedure involves attaching soluble polymer molecules to the particle surface. Under suitable conditions, and with a sufficient surface density of chains, the polymer layers will induce a repulsion potential between the particles. Using a characteristic magnitude of the potential and the thermal energy kT a ratio can be calculated which provides a dimensionless expression Ψ_d for the repulsion (Russel et al.²):

$$\Psi_d = ar_g^2 n_b / N \quad (4)$$

where r_g is the radius of gyration, n_b the segment density and N the number of segments in the polymer chain. For polymerically stabilized systems one thus expect for the viscosity a relation:

$$\eta_r = f(\sigma_r, \Psi_d, \phi) \quad (5)$$

where ϕ is the particle volume fraction.

VISCOSITY CURVES

Stable colloidal dispersions are characterized by viscosity curves displaying two Newtonian plateaus separated by a shear thinning zone. They can be described quite well by:

$$\eta = \eta_\infty + (\eta_0 - \eta_\infty) / [1 + (\sigma_r / \sigma_{rc})^m] \quad (6)$$

where the characteristic relative stress σ_{rc} , the limiting Newtonian viscosities η_0 and η_∞ and the factor m determine the curve. The concentration dependence of the limiting viscosities can be expressed by the Krieger-Dougherty equation:

$$\eta_r = [1 - (\phi / \phi_{max})]^{[\eta]\phi_{max}} \quad (7)$$

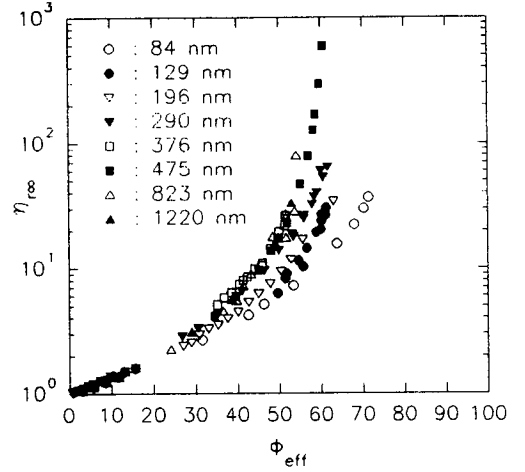


Figure 1: Newtonian high shear viscosities for several particle sizes

where $[\eta]$ is the intrinsic viscosity and ϕ_{max} the volume fraction at which the viscosity diverges. Systematic data are available for suspensions of poly(methylmethacrylate) (PMMA), (12-hydroxystearic acid), chemically grafted on the particle provides a polymeric stabilizer layer (thickness 9 nm) (Mewis et al.⁶, Mewis and D’Haene⁷). For polymerically stabilized systems it is difficult to characterize the stabilizer layer sufficiently to calculate Ψ_d . Therefore one attempts to derive alternative characteristics from the rheological data.

Different procedures can be used, depending on the relative thickness and the softness of the stabilizer layer. When its thickness δ is much smaller than the particle radius, the suspensions should behave as those of Brownian hard spheres. The volume of the stabilizer layer may not be totally negligible with respect to the particle volume. This can be corrected by assuming hard spheres with a radius $a + \delta$ and an effective volume fraction ϕ_{eff} calculated on this basis. The value of the latter is obtained from a comparison between the measured intrinsic viscosity and the theoretical value of 2.5 (“hydrodynamic layer thickness”).

If the said procedure works the relation between the Newtonian viscosities and the effective volume fraction should be independent of particle size. From figure 1 it

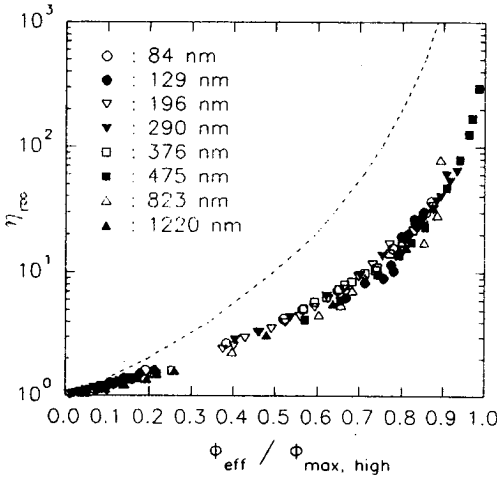


Figure 2: Limiting high shear viscosities as a function of ϕ_{eff}/ϕ_{max}

can be seen that this is not the case except at the largest particle sizes. The volume at maximum packing increases with increasing δ/a and is larger than that for hard spheres. Clearly the soft stabilizer layer gets compressed in this case.

As a second approximation one can assume that the $\eta(\phi_{eff})$ relation can still be represented by eqn. (7) but that ϕ_{max} depends on the softness of the stabilizer layer. In that case the curves for sterically stabilized systems would still coincide with those for hard spheres if they are plotted as a function of ϕ_{eff}/ϕ_{max} . Figure 2 indicates that this procedure is quite adequate for the systems under consideration. Obviously it should fail for very thick, soft stabilizer layers or for soft particles. Such systems could give rise to effective volume fractions larger than unity. The dotted line in fig. 2 illustrates this behaviour for a sample with a thick (36 nm) stabilizer layer, it can also be seen in the data by Wolfe and Scopazzi⁸ on microgels. The concentration dependence of the viscosity then gradually shifts from that for suspensions of hard spheres to that of polymer solutions.

DYNAMIC MODULI

Colloidal dispersions are also viscoelastic. In Brownian hard spheres the thermal motion entails "memory" and elastic

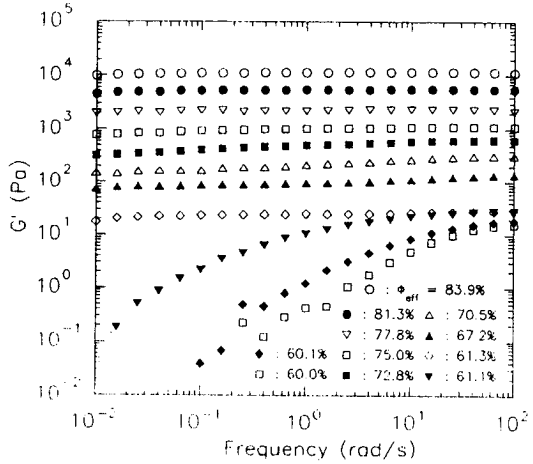


Figure 3: Storage moduli for PMMA particles ($a=65\text{nm}$)

effects. In sterically stabilized systems the compression of the stabilizer molecules causes elastic interparticle forces. At volume fractions where the stabilizer layers overlap, this should give rise to elastic contributions such as storage moduli in oscillatory experiments (Frith and al.⁹). The result of such measurements is displayed in figure 3.

At low frequencies thermal motion is faster than the convective motion and liquidlike behaviour is observed (see low frequencies and low concentrations in fig. 3). At high frequencies the moduli probe the particle interaction and hence stabilizer layer softness. If the relative positions of the particles were known, the modulus-concentration curve could in principle be transformed into a relation between potential and interparticle distance. Assuming that the distance between particles equals everywhere the average value gives the same potential profile for the different particle sizes (D'Haene and Mewis¹⁰). Hence the result is expected to be physically meaningful.

The storage moduli and the interparticle potential are measures of the softness of the stabilizer layer. From the interparticle potentials the distance of closest contact can be calculated. It can be considered an effective hard sphere diameter, from which the corresponding effective hard sphere volume fraction $\phi_{eff,h}$ can be

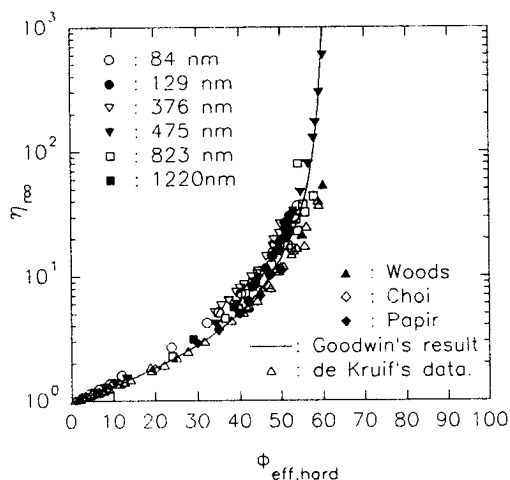


Figure 4: Limiting high shear viscosities as a function of the effective hard sphere volume fraction

derived. The result is shown in fig. 4. The data for the different particle sizes superimpose well in this manner. It is concluded that the moduli can indeed be used to predict the softness effect and thus the concentration dependence of the viscosity.

CONCLUSIONS

Polymerically stabilized dispersions differ from Brownian hard spheres in that a deformable polymer layer is present at the surface. Because of this the usual scaling laws for Brownian hard spheres do not apply, neither for the viscosities nor for the dynamic moduli. If the stabilizer layer is not extremely soft the major difference with hard spheres, for the viscosities, is the maximum packing volume. The storage moduli display a high frequency plateau which probes the particle interaction forces and thus the deformability of the stabilizer layer. From the moduli the interaction potential can be computed, which in turn provides a means to calculate the maximum packing and the viscosity curves.

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