The Diabolical Case of the Recurring Yield Stress

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ABSTRACT

The yield stress has, since its conception, been a source of fierce and often acrimonious debate. This review article deals with the issue, looking at problems related to the meaning of the definition, timescale of the observation, whether the yield stress is a property of concentrated suspensions or is linked to the strength of coherent network structures. We discuss the problematic nature of how to measure the yield stress, directly or indirectly, and examples of the vane geometry are given. Throughout, absolutist and realist theories and evidence are presented and a consensus is finally drawn. Rheologists should embrace the consequences of the absolutist and realist theories and apply them to their everyday world – whatever the timescale!

HOLMES' PARLOUR 221B

Waiting for Holmes to return, I was tucking into some of Mrs. Hudson's heavenly crumpets and tea. I had the intention of discussing that irritable yield stress thing that has so plagued the rheological world since Bingham (1920) came up with the term. So many references to it exist.

I took the trouble before visiting Holmes to search for "yield stress" on Google and came up with 591 000 hits, whilst a more specific search of "yield stress, rheology" gave 6130! While biting into my second crumpet, the door opened and in walked Holmes.

"Ah, Watson, my dear fellow, what brings you here today, and already on your second crumpet I see." said Holmes.

"Ah, Holmes, eh yes, I came to discuss the yield stress phenomenon with you." I blurted out. "But how did you know it was my second crumpet, lucky guess I suppose." I said.

"Watson, I never guess, I deduce, and I can see from the level of flour on your plate and your sleeve that two of Mrs. Hudson's crumpets are required." barked Holmes. "Anyway, to business, the yield stress you say."

"Yes Holmes, I find the whole thing a shade confusing if I am to be honest. First one person says one thing and then another says something completely different, and all with the supposed security of a decent bit of research behind them." I exclaimed. "In my own medical profession we don't have much use for the term and I think the whole thing degenerates into hogwash pretty quickly." I continued.

"Hogwash you say Watson, harsh words indeed. True enough, there has been a large and often acrimonious debate within the rheological world on this topic, much of it I have to say rather esoteric and confined to basic misunderstandings or indeed misuse of language." proclaimed Holmes.

I was aware of the debate that had raged in the rheological world for many years now, and having read a bit I decided that the yield stress was bunk, but I was still not quite sure what Holmes was driving at with his esoteric and misuse of language statement. Surely both camps could not be

right and wrong at the same time? It certainly appeared as though this was what he was suggesting, or was there something more?

"You see Watson, what is called for in the yield stress debate is a clear head first and foremost. It is worth remembering a small piece of wisdom given to us by Bacon back in 1605, "The mind of man is far from the nature of a clear and equal glass, wherein the beams of things should reflect according to their true incidence; nay it is rather like an enchanted glass, full of superstition and imposture, if it be not delivered and reduced."" exclaimed Holmes.

"Quod enim mavult homo verum esse, id poitus credit. I believe you mean" I said.

"Watson, precisely. Brilliant. "What man wishes were true, he more readily believes. I feel we can now enter the yield stress debate with objectivity and credence of conscience required to progress." said Holmes.

"Firstly Watson, we must be sure we agree what we mean by yield?"

"Why not take the definition given by Barnes, "to give way under the application of excessive force."" I said.

"Splendid Watson, and if we continue this theme to yield stress we find that in 1985 our dear friend Barnes, along with Walters said, "that stress below which the substance is an elastic solid and above it a liquid with a plastic viscosity."" said Holmes.

There was nothing new in this definition of the yield stress, but it did rather imply an absolute, I was thinking. If one was to continue with this absolute, where would it lead and what were the consequences? Indeed, should such an absolute be countenanced? Infinite viscosity – balderdash! Feeling quite pleased, I could see that Holmes was obviously taking my side of the argument.

"Doesn't such a definition rather imply an absolute, Holmes?" I questioned smugly.

"Indeed Watson, or should I say absolutely!" chuckled Holmes. "I have here Watson" Holmes continued, "the paper by Scott Blair of 1933 where he states of the yield stress, "that stress below which no flow can be observed – under the conditions of the experiment.", which immediately introduces a question and removes the absolute that you mentioned." said Holmes.

This seventy year old citation introduced an element of doubt into the whole debate, and I could already feel that I was on shaky ground. After all the absolute suggested by the first yield stress definition suggested that below a certain stress the viscosity of the measured system tended towards infinity! This tendency towards infinity was as true for ketchup as it was for glass. Clearly rubbish, but now Holmes had thrown doubt into the ring.

"What are you saying Holmes, that the yield stress is a result either of limited data or by instrumental limitations?" I asked.

"Why, both Watson, depending on either the conditions set or the instrument used. Think back to our review a couple of years ago (Watson, 2001) detailing the progress in rheometers. Clearly instrument limitation was a key factor not so long ago." Holmes exclaimed.

"Why, Holmes, that would suggest nobody has ever measured a yield stress, simply extrapolated to it" I asked, feeling much better with myself..

"One could think of it that way Watson, but I think it fair to look into what others have said about the yield stress." said Holmes. Continuing, Holmes said. "Duzy & Boger 1983 stated that the yield stress is a rheological property that all highly concentrated suspensions may have in common, and that precise knowledge of the yield stress is important in handling, storage, and transport of such suspensions. Then, Buattacharya in 1999 said the yield stress is not only related to the strength of coherent network structures, but also is important to

estimate coating thickness, drip reduction of coatings, preventing flow and impeding the settling of suspended fine particles."

"Surely Holmes, we are simply talking about timescales, particularly timescales of measurement. Indeed I have read that the measurement of the yield stress is simply the measure of the experimenter's patience – or lack of!" I said somewhat pleased with myself that my absolutist theory was holding up to Holmes' interrogations.

"Ha, Watson, very good, but consider this, unlike your good self we do not all have the patience of Job nor the time to wait. Some applications take place over short timescales and the apparent non flow of a material may be an important fact." Holmes exclaimed. "And, Watson, were you paying attention to my use of the word 'apparent'?" he asked.

"But Holmes, what are you saying? I can never fathom if you believe in this ridiculous yield stress theory or not."

"Watson, it is not a question of belief, it is a matter of using ones data to suit ones conditions. Consider the ketchup problem again, by the time I wait for it to flow out of the bottle alone, my food is likely to be cold, but if I am enjoying a salad and am prepared to go hungry for a while, wait I might and be rewarded with the ketchup on my plate." Holmes stated. "What one must do is focus on the point of ones measurement and not begin to make claims for the data out with the parameters being measured."

"And what then is your point Holmes?" I asked.

"Well, Watson, statements like everything flows and its Greek equivalent, "παντια ρει", taken from Heraclitus and indeed Deborah's, "The mountains melted before the Lord." from the Old Testament book of Judges are all very well, but they don't help someone facing material problems occurring over timescales of minutes or hours as opposed to centuries or the aeons of geologic time."

"Are you claiming then Holmes, that the yield stress is a valid parameter that can play a role in predicting material properties? After all, we accept that particle suspension is probably better expressed and understood by using Stokes law (Young, 2002)." I asked.

"Within limits Watson, within limits. However, what is also important, and not something we have discussed yet, is how best to measure, or should I say estimate our yield stress value." Holmes said.

"The important thing Holmes," I said, still arguing against the yield stress, "is to try and avoid slip, and that usually it is best to measure using controlled stress conditions than controlled strain. Under controlled strain conditions, the instrument applies a strain and measures the resultant stress, but one is uncertain if the initial strain was destructive. One also has to consider, for samples with very low yield stresses that the air bearing offset torque value is not the same as the yield stress itself."

"Exactly Watson, for an anti-yield stress man, you have a remarkable knowledge instrumentation." said Holmes smiling. "Occasionally you excel yourself when least expected. As you rightly suggest yield stress measurement is not easy, but you neglected to mention that the parameter can be measured either indirectly or directly! The indirect method's basis is interpretation of fundamental shear stress – shear rate data in an attempt to obtain the shear stress in the limit of zero shear rate. The technique itself is simple and straightforward, but suffers from the usual lack of data at sufficiently low shear rates, and even supposing we have this low data Watson, as you rightly pointed out, slip may have occurred thus making our data unreliable.

Now, for direct measurement, this can take place either in controlled stress or controlled strain formats. Either one uses controlled stress, applying a constant stress

and observing the resultant deformation as a function of time, whereas….."

"Ah, Holmes, dear fellow, is that not what I said?

"In essence Watson, in essence, but one must learn to be precise." Holmes said, somewhat irritated.

"And one should learn to listen Holmes." I said, smirking.

"Well then Watson, since you're such an expert, perhaps you'd like to elaborate on the most popular method to detect yield stress?" said Holmes.

It was clear that I had annoyed him by interrupting and I would have to be careful not to be on the wrong end of his wrath or intellect. Fortunately, I had read a bit about this vane geometry after I'd found a paper by Barnes and Carnali (1990), where they used the vane to show the absence of any yield stress. However, there was a paper by Dzuy and Boger (1985) claiming that the vane was capable of direct yield stress measurement and it was this paper that I quoted now.

"I think you'll find the vane geometry gives a good account of itself in providing a direct measurement for true yield stresses under virtually static conditions, eliminating slip, causing minimum disruption to the sample and by applying the fundamental concept of the yield stress as a true material property associated with the strength of a continuous three dimensional network within the system." I said, sitting back in my chair rather smug with myself.

"Very good Watson, you're not suddenly becoming pro-yield stress are you? And I suppose you propose to tell me now how the vane works with respect to the sample." asked Holmes, clearly annoyed that I seemed to be in control.

It was at times like these that I knew I had to be careful and that he would probably have an ace up his sleeve. But it was so difficult to stop once I got into my stride, despite the feeling that there was a trap waiting round the metaphorical corner.

" No Holmes, I stick to my principles, but, if we talk about concentrated suspensions,(Dzuy & Boger, 1983) as the vane rotates, the suspension close to the edge deforms elastically, seen as a linear response in the torque – time curve. Of course any material between the vane blades moves with the vane. Such linear behaviour was attributed to stretching of network bonds, interconnecting structural elements. As more bonds were stretched the resistance to deformation increased with the vane's continued rotation. Hence, the torque required to keep the constant motion also rises. Finally, breaking of the bonds must similarly occur, and when all, or the majority of these network bonds have broken the network collapses and microscopically the sample can be said to have yielded. This yielding may be irreversible due to weak hydrodynamic forces at the low shear rates being insufficient to allow the network bonds to reform. Therefore Holmes, this was taken as explanation of the maximum in torque value and followed by a rapid decrease in the torque from the torque-time curve. Not only that Holmes, but in 1985 the same two workers reported that it could be reasonably assumed that there was a uniform stress distribution everywhere on the sheared surface. This, they noted was only valid though precisely at the moment of yielding and did not occur before or after." I said.

"Well Watson, an impressive collection of statements indeed, and one that is difficult to find fault with. I think you'll agree that in 1987 James and co-workers reported similar findings and stated that the absence of slip when using the vane allows the material to yield within itself." said Holmes.

"Indeed Holmes, but what do you make of the paper by Barnes and Carnali (1990) who looked at the vane geometry and by

means of numerical analysis showed that the yield stress did not exist?" I exclaimed, grinning. Continuing, "They claimed, in comparison with a bob geometry, that the flatter stress profile obtained with the vane geometry postponed the formation of a thixotropic layer at the surface of the vane, which they indicated could lead to apparent slip. Thus, with the removal of this possibility they still produced data indicating the onset of the low shear Newtonian plateau and therefore suggested the absence of a true yield stress. You see, Holmes, the existence of a yield stress implies that nothing is happening to the sample at these low stresses. Indeed, as much is happening below the yield stress as there is above. If a sample will flow at high stresses then it will most certainly flow at low stresses – just very slowly. Creep I believe one calls it. Plenty of samples thought of as yield stress systems are simply very shear thinning systems, often with viscosity dropping by up to a million fold over the space of one decade of stress.

"Watson, I have to say, you are quite correct, but I fear that you are still applying a somewhat absolutist approach to your argument." Holmes said.

"But Holmes, any system capable of a relaxation mechanism cannot, by definition, be capable of a yield stress. There is always some method by which, at the molecular scale, movement and thereby flow can take place, assuming of course we are above absolute zero Kelvin." I said. "This is true for all materials."

I felt as though the weight of evidence against the yield stress was in my favour and that I may in fact win this debate.

"Watson, let me show you what a dangerous state we have got ourselves into here. Do you remember the paper in 1995 by Spaans and Williams? Holmes asked.

"Erm, no, not really Holmes, was there not some claim made that they had a system without a relaxation mechanism? I said.

"Well, not quite Watson, they used the Erying rate theory to try and imply that imposing a stress lowers any potential barrier to molecular movement in the direction of the stress, but raises the barrier in the opposite direction. Now, if this were the case, as our friend Barnes (1999) pointed out what a marvellous discovery it would have been. They would have found the only substance in the universe that does not conform to the fundamentals of continuous creep!"

" I see, but Holmes, does it not seem that we are beginning to go round in circles with this debate now? After all have we not agreed that there is no fundamental yield stress. If one must refer to one then it should be in terms of an apparent yield stress." I said.

"Yes and no Watson, I was beginning to think that not only are we going round in circles, but that we may soon start bickering at each other like the most ignoble of politicians. I feel that we must begin to conclude our discussion and learn to accept, moving away from the semantics of the argument, that both camps are right and both camps are wrong!" stated Holmes.

"Both right and both wrong Holmes, you'll be telling me next that I'm Schrödingers cat!" I exclaimed.

"Watson, clarity, not hilarity is required at such a stage. I think you'll agree that we need to use our heads and our pragmatism in confronting this problem that really need not be a problem at all." said Holmes. "It basically comes down to what language we use and what we understand by that language. Evans in 1992 said as much that the 'classical' definition used by Barnes and Walters in their 1985 paper basically defines the yield stress out of existence, whereas if one chooses a practical approach defining the given strain sensitivity and time scale of the measurement one has basically defined the yield stress into existence." continued Holmes.

"Defining into or out of existence Holmes, really you exasperate me sometimes, what sort of conclusion am I supposed to draw from that?" I asked.

"Elementary my dear Watson, having been faced with incorrect or inaccurate definitions since its conception, the rheological world has raised its own storm in a tea cup. What they should be doing is leaving the esoteric semantics alone and concentrating on what they do best – rheology! They only need to carefully define their measurement parameters, not go making rash claims for the data out with the measurement range and they can happily use their yield stress values and principles. However, Watson, a word of caution to them, any application concerned with sedimentation would do well to heed the controversial arguments proposed as it is more than likely that creep forces will ultimately dominate." said Holmes. " Now let's finish up here with another cup of tea and a crumpet before going to the Strand Hotel where I have an appointment with a young woman concerning a red headed league. Will you join me Watson?

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REFERENCES

Bacon, F. (Original 1605) "The advancement of learning." (eds. Spedding, J., Ellis, R.L. and Heath, D.D.) *Works* 15vols., Cambridge MA (1863), vi.327.

Barnes, H.A. (1999) "The yield stress - a review or 'παντπ ρει' - everything flows." *J. Non-Newtonian Fluid Mech.* **81**, 133-178.

Barnes, H.A. and Carnali, J.O. (1990) "The vane-in-cup as a novel rheometer geometry for shear thinning and thixotropic materials." *J.Rheol.* **34**(6), 841-866.

Barnes, H.A. and Walters, K. (1985) "The yield stress myth." *Rheol Acta* **24**, 323-326.

Bhattacharya, S. (1999) "Yield stress and time-dependent rheological properties of mango pulp." *Journal of Food Science*, **64**(6), 1029-1033.

Bingham, E.C. and Green, H. (1920) "Paint, a plastic material and not a viscous liquid; the measurement of its mobility and yield value." *Proc. Am. Soc. Test Matl.* **20**, 640-675.

Dzuy, N.Q. and Boger, D.V. (1983) "Yield stress measurement for concentrated suspensions." *J. Rheol.* **27**(4), 321-349.

Dzuy, N.Q. and Boger, D.V. (1985) "Direct yield stress measurement with the vane method." *J. Rheol.* **29**(3), 335-347.

Evans, I.D. (1992) "Letter to the Editor: On the nature of the yield stress." *J. Rheol*. **36**(7), 1313-1316.

James, A.E., Williams, D.J.A. and Williams, P.R. (1987) "Direct measurement of static yield stress properties of cohesive suspensions." *Rheol Acta* **26**, 437-446.

Scott Blair, G.W. (1933) "On the nature of "yield-value"." *Physics*. **4**, 113-118.

Spaans, R.D. and Williams, M.C. (1995) "At last a true liquid-phase yield stress." *J. Rheol.* **39 (1)** 241-246.

The Bible, King James Version. Judges, Chap.5 verse 5.

Watson, J.H. (2001) “Decades of progress: The shifting boundaries of rheometers.” *Annual Transaction of the Nordic Rheology Society* **9**, 89-96.

Young, N.W.G. (2002) “The yield stress phenomenon and related issues – An industrial view.” *Gums and Stabilisers for the Food Industry 11*, Eds. Williams, P.A. and Phillips, G.O., Royal Society of Chemistry. 226-234.