This document is meant to encapsulate the discussion from Thursday July 9th 2009 on the review of the paper:

"No steady state flows below the yield stress. A true yield stress at last?"
-Møller, Fall, Bonn (ArXiv: 0904.1467v1 cond-mat.soft)

Additional reading (in order of helpfulness):

-"'The yield stress myth' revisited" H A Barnes appearing in: Moldenaers P, Keunings R (eds) Theoretical and applied rheology. Proceedings of the XIth International Congress on Rheology, Brussels, Belgium, August 17-21, 1992, pp 576-578

-"Yield stress and thixotropy: on the difficulty of measuring yield stress in practice" Møller, Mewis, Bonn Soft Matter 2006 2 274-283

-"Letter to the Editor: a true yield stress" De Kee, C.F. Chan Man Fong Journal of Rheology 37 (4) July/August 1993

The following report has 7 sections:

- Brief Overview of Paper
- Remarks on Claims in the Paper
- Further Thoughts on Thixotropy, Yield Stress and the Aging vs. Rejuvenation Picture
- Next Questions on Relating a Time Dependent Viscosity to Previous Models
- Can a Rheometer Measure an Infinite Viscosity Below a Yield Stress?
- Pondering Dimensionless Numbers to describe Yield Stress Fluids
- Remarks on Presentation of Paper

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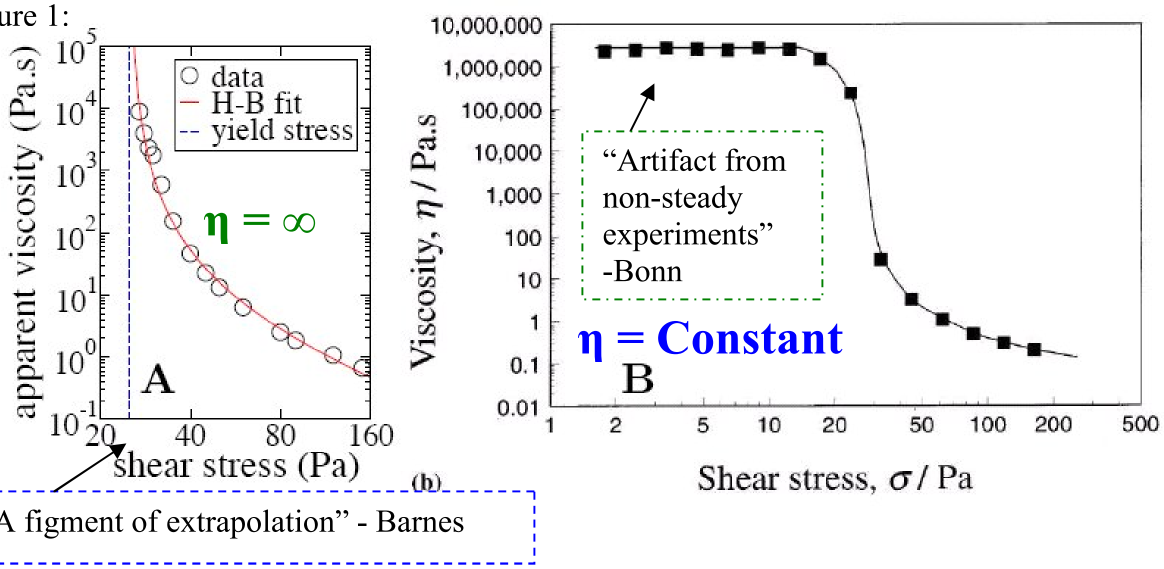
Brief Overview of the Paper

The objective of the paper is to address whether the yield stress is a transition between a solid state and a liquid state or a transition between a liquid state and another liquid state (as advocated by Barnes and Walters).

This distinction is made by comparing two different ways of presenting data and assigning a value to viscosity to inaccessible shear rates.

Figure 1:



"Artifact from non-steady experiments" -Bonn

"A figment of extrapolation" - Barnes

Graph A represents Bonn's view that the material transitions from a solid (**η** = ∞) to a liquid and Graph B represents Barnes's view that it transitions from a liquid (**η** = finite) to another liquid, albeit dissimilar from the first regime.

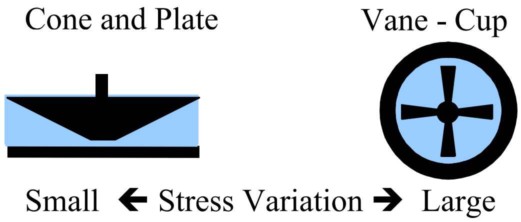
The authors present evidence for their solid-liquid transition view by replicating Barnes's rheological testing protocol on four carbopol based materials. They perform creep tests, where a constant low stress is applied to the material and the resulting deformation and flow is monitored over the period of the test. They argue that they have eliminated many common artifacts encountered with testing yield stress materials, such as wall slip, by using a variety of different rheometer/geometry combinations. Their results are consistent across these many tests in that they do find that there is a plateau viscosity at very low shear rates. If, however, they vary the amount of time they spend collecting this viscosity, they find that this plateau viscosity increases indefinitely with time. They conclude that the Newtonian viscosity plateau is an artifact of the measurement being collected before the system reaches steady state.

The authors then discuss possible microstructural reasons for this viscosity increasing with time. They note that this behavior may have been expected if the material were aging and structuring with time. However, the materials in this study do not fit a traditional definition of thixotropy. The material does not age when at rest and the flow history (at high shear rates) does not influence the material behaviour. They suggest that the very low shear rate could change the balance between forming connections and breaking connections by supplying enough energy to bring particles together where for 'true' yield stress materials thermal forces would suffice. With this, they offer an alternate definition of the yield stress as one between aging and rejuvenation.

Remarks on Claims in the Paper

Materials: The authors suggest that the four materials that they have tested are a representative sample of yield stress materials. **However all four of the samples are in fact all carbopol based and fall into a small category of non-classically-thixotropic yield stress materials**. While the authors extend their conclusions to yield stress materials in general we might question this generalization. The authors also cite that carbopol foams and emulsions are normally not considered as materials that age and therefore explain all aging seen at rest as due to low-shear induced. Further work should be done to examine this assumption as their measurement protocol has an unusually long duration. For instance, they report elsewhere that their foam coarsens over a period of 8 hours from a bubble size of 12 μm to 50 μm. This time period is on the same order of magnitude as their 3 hour creep tests.

Shear banding: The authors claim that shear banding, or shear localization, in non-thixotropic yield stress fluids happens only if there is significant stress variation within the geometry. As they used geometries that have very different stress variation profiles the authors state that shear banding is not an issue in their results.



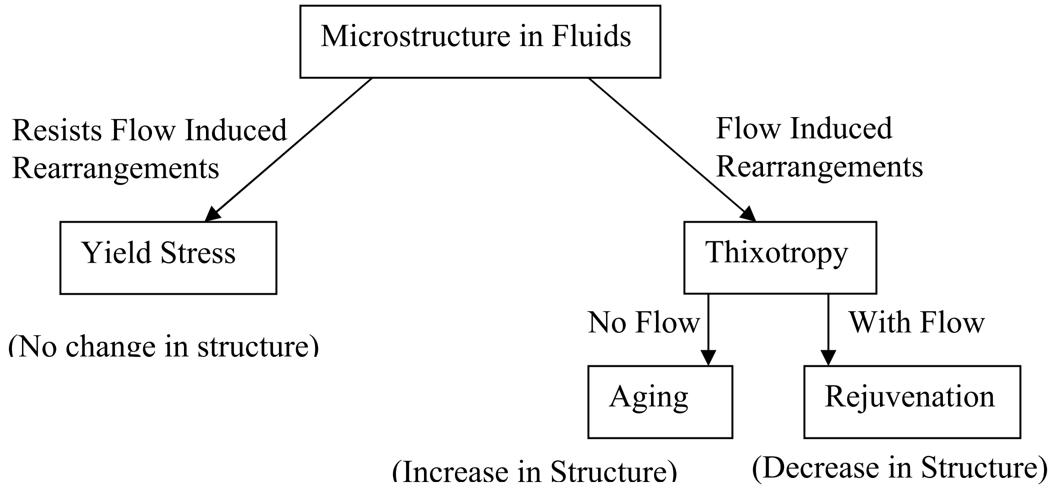
However, in light of their argument that the fluid ages during low shear flow experiments, it may be more accurate that shear banding does occur and is due to "age" inhomogenieties intrinsic to the fluid.

Comparison to Barnes: In the '"Yield Stress Myth?" Revisited', Barnes does suggest suspensions that might be expected to have yield stresses. These suspensions, including simple 'non-interacting' suspensions and flocculated suspension, seem similar to the scenario that Bonn presents. **Barnes suggests that we can expect a yield stress when dealing with suspensions that may achieve a phase volume of particles equaling a maximum phase volume when the particles are densely packed.** Given that this paper is written to address many of Barnes's findings, it would make sense to investigate the model suggested by Barnes to explain the appearance of a yield stress in a flocculated suspension.

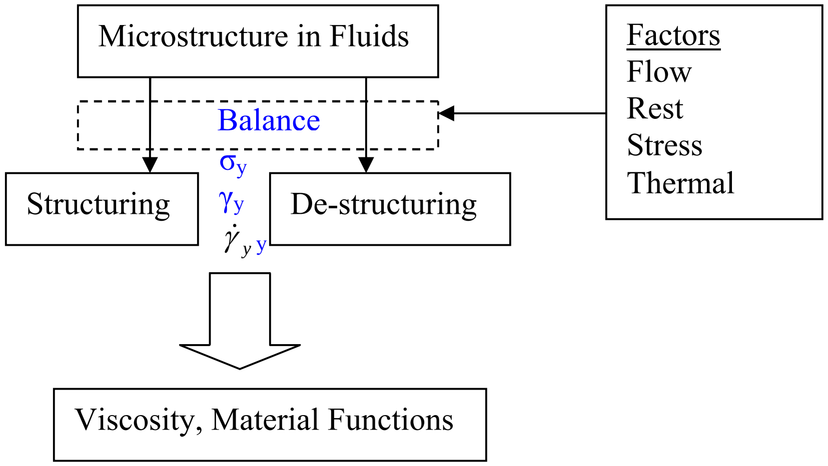
Infinitely Increasing Viscosity: The authors suggest that the viscosity of their fluids will increase exponentially ($\eta \sim t^{u}$) with time. They further use their low-shear aging explanation to support their observation of a growing viscosity. **A closer examination of the physical picture however, does not support a viscosity that increases with time *<u>without bounds</u>*.** With Barnes's picture of a yield stress being a state of maxed packing, we can imagine that there is a time where the particles reach the required packing density. At this time we would expect that the viscosity plateau should be measured as infinite. The authors must decide whether the viscosity plateau and its time dependence, is one of measurement error from lack of patience or from actual structural kinetics. The picture involving kinetics suggests that at some point the material does indeed reach steady state by the limit of the number of connections that can be made by a finite number of particles.

Further thoughts on Thixotropy, Yield Stress and the Aging vs. Rejuvenation Picture

The following picture seeks to capture current relationships between yield stress and thixotropy vocabulary.



This picture however is incomplete, as Bonn points out that this picture does not allow for a fluid to "age" in the presence of shear flow rather than at rest. Bonn's fluids are the first reported fluids that age when under low flow but not at rest. Bonn's microstructural picture suggests that the yield stress is not as an intrinsic variable, but rather depends on the nature of the volume of fluid over which it is evaluated. **This volume of fluid is experiencing a balance of processes both structuring and de-structuring the fluid.** Fluids made of very small particles, structure at rest because of thermal forces. However for larger particles, both the nature of how we probe the system and de-structuring processes usually dominate. We rarely observe a fluid that does not change its structure or increases its structure while still being loaded. A thought experiment that would measure this alternate definition of a yield stress could be that imposing **a stress which equals the yield stress would prevent structuring in a fluid, which at rest, ages**.



If material is structuring ➔ Increase in viscosity
If material is de-structuring ➔ Decrease in viscosity

By more closely relating thixotropy and yield stress, we could seek less controversial definitions of both.

Next Questions on Relating a Time Dependent Viscosity to Previous Models

The microstructural picture presented by Bonn is not new. Mujumbar summarizes models that attempt to balance the kinetics of building and breaking bonds with the expression:

$$-\frac{dn}{dt} = k_{-}n(\dot{\gamma})^{a} - k_{+}(n_{0}-n)(\dot{\gamma})^{b}$$

n is the number of active bonds
n₀ is the number of initial bonds
k_- is the rate of structure breakdown
k_+ is the rate of structure build-up
$\dot{\gamma}$ is the shear rate

In a previous paper Bonn presents an evolution equation:

$$\frac{d\lambda}{dt} = \frac{1}{\tau} - \alpha\lambda\dot{\gamma}$$

$$\eta = \eta_{0}(1+\beta\lambda^{n})$$

λ is a measure of the number of connections per unit volume
τ is the characteristic time of the build-up of the microstructure at rest
η_0 is the limiting viscosity at high shear rates
α, β, and *n* are material constants

Solving these equations for the time evolution of the structure parameter we find (respectively):

$$n = n_{0}(\exp((k_{-}\dot{\gamma}^{a} + k_{+}\dot{\gamma}^{b})k_{2}n_{0}\dot{\gamma}^{b}t))$$

$$\lambda = \frac{1}{\alpha\tau\dot{\gamma}}\left(1+[\tau\lambda_{0}-1]e^{-t/\alpha\dot{\gamma}}\right)$$

Neither of these time evolutions combined with associated viscosity models suggest a viscosity that grows as $\eta \sim t^{\mu}$.

If the time dependence in the inset graphs, really reflects "aging under stress" and not impatience – a next step would be to compare this time prediction with an appropriate model.

Barnes's picture of flocs growing and particles jamming to progressively form larger structures provides a second mental test to judge whether the viscosity growing in time without bound is physically realizable.

Can a Rheometer Measure an Infinite Viscosity below a Yield Stress?

The rheometer has both a smallest and largest torque that it can measure. This limits the resolvable viscosities in a given amount of time. If there exists a yield stress at which the viscosity of the fluid becomes infinite, would a rheometer take an infinite amount of time to report this viscosity?

$$\eta_{\max} = \frac{\sigma_{\max}}{\dot{\gamma}_{\min}}$$

$$\eta_{\max} = K_{geometry} \frac{T_{\max}}{\Omega_{\min}}$$

$$\eta_{\max} = K_{geometry} \frac{T_{\max}}{\theta_{\min} / t_{scientist}}$$

For the AR-G2[1]:

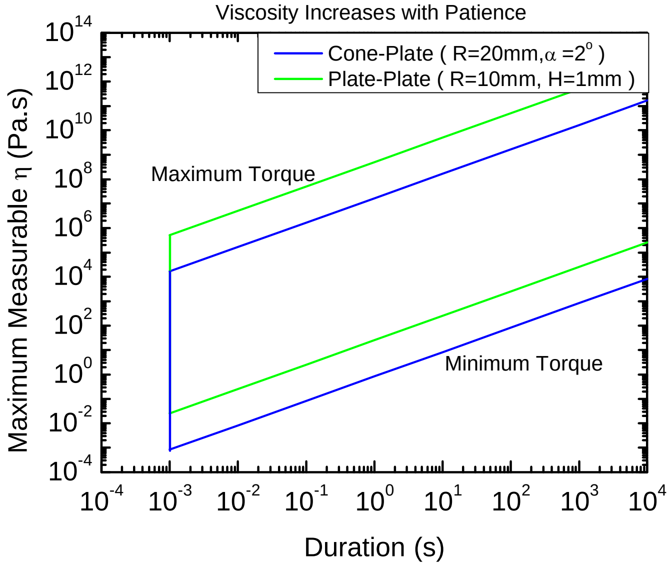
T_{max}=200e-3Nm
θ_{min}=25e-6 rad

For a typical cone and plate (R=20mm, α=2°):

$$\eta_{\max} = \frac{3\alpha}{2\pi R^3} \frac{T_{\max}}{\theta_{\min} / t_{scientist}} = \frac{3 * .035}{2\pi (20e-3)^3} \frac{200e-3}{25e-6 / t_{scientist}} = 1.7e7 * t_{scientist}$$

For a typical plate and plate (R=10mm, H=1mm):

$$\eta_{\max} = \frac{2H}{\pi R^4} \frac{T_{\max}}{\theta_{\min} / t_{scientist}} = \frac{2 * 1e-3}{\pi (10e-3)^4} \frac{200e-3}{25e-6 / t_{scientist}} = 5.1e8 * t_{scientist}$$



Note that the rheologist may choose any torque between the minimum and maximum limits for various reasons, such as not wanting to destroy existing microstructure.

Given that the time evolution of the viscosity seems to match a trend related to protocol more closely than trends related to microstructural models, perhaps this phenomena is indeed a measure of patience.

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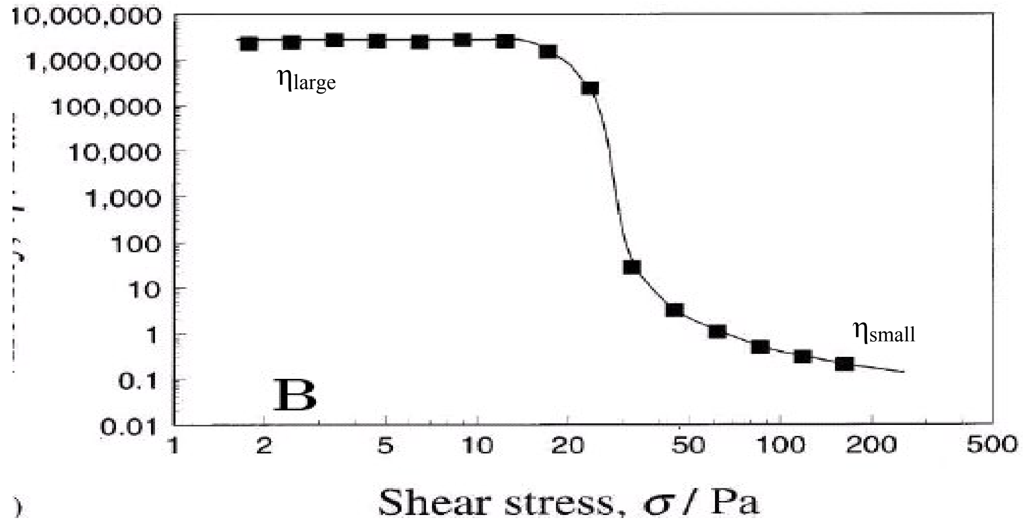
[1] TA Instruments specifications at http://www.tainstruments.com/product.aspx?id=43&n=1&siteid=11

Pondering Dimensionless Numbers to Describe Yield Stress Fluids

Barnes's insistence on a rigorous approach of not allowing approximations about the material behavior even if the material does not seem to flow on the timescale of months seems disconnected from engineering applications. Information on the time scales of use and load upon the material is relevant to selecting an appropriate material. **An engineer might argue that the controversy surrounding the yield stress does not change the existence of an applied stress below which the material does not appear to flow.**



This engineer might want to describe whether this fluid is a suitable yield stress material, despite the controversial nature of the definition of the yield stress. **What dimensionless number might we equip him with to describe how "yield-stressy" a fluid is?**

The Bingham Number, does not seem to capture this desire $Bm = \frac{\sigma_y L}{\eta V} = \frac{Yield\_Stress}{Viscous\_Stress}$

We could incorporate variables such as $\Delta\eta$, η, λ, σ_y, G', G", $t_{experiment}$, and desired applied stress into a different dimensionless numbers using Buckingham PI theorem.

One suggestion might be: $\tilde{L} = \frac{L_{flow}}{L_c} = \frac{\sigma_{appl} t_{duration} h}{\eta_{\sigma_{appl}} L_c}$

h is the thickness of the film

σ_{appl} is the applied stress during the experiment

$t_{duration}$ is the duration of an experiment or application

$\eta_{\sigma_{appl}}$ is the viscosity corresponding to the applied stress

L_c is a characteristic length scale appropriate for the duration of the experiment

$\tilde{L} \ll 1$ material is solid-like; no observable flow on the experimental scale

$\tilde{L} \sim 1$ observable flow on the experimental scale

$\tilde{L} \gg 1$ material is fluid-like; flow dominates experiment

This number compares the distance the material will flow to a characteristic length of an experiment.

This number may be helpful to describe application requirements and experimental results.

Application Case Study: Adhesive Locomotion
The relevant length scale might be related to the stroke length of the robotic motion or the length of the robot. The time would be the time associated with the period of the stroke. Interestingly, this number could be useful for fluids that are typically not described as having a yield stress but can be used as if they are yield stress materials for experiments that have short time scales or large characteristic length scales (such as the example detailed above).

Experimental Case Study: Bonn's Results
This number could also describe experimental results. For instance, Bonn's material could be described as having $\tilde{L} \le 1$ for characteristic length scales up to 27 microns. By using this number to describe both experimental results and applications we can have increased confidence that we have picked an appropriate fluid for a given application.

Finally, this number can help define a yield stress material even in more theoretical situations. If $\tilde{L}$ approaches zero the material would be a "true yield stress" material. A material that ages as $\eta \sim t^n : n < 1$ as Bonn suggests would not meet this definition; materials that age faster than this would.

$$\tilde{L} = \frac{\sigma_{appl} t_{duration} h}{\eta_{\sigma_{appl}} L_c}$$

$$\eta = \eta_0 \left(\frac{t}{\lambda} \right)^n$$

$$n = 1$$

$$\tilde{L} = \frac{\sigma_{appl} t_{duration} h}{\eta_0 \left(\frac{t_{duration}}{\lambda} \right)^1 L_c} = \frac{\sigma_{appl} \lambda h}{\eta_0 L_c}$$

$$n < 1$$

$$\tilde{L} = \frac{\sigma_{appl} \lambda^n h}{\eta_0 L_c} \left(t_{duration}{}^{1-n} \right) \xrightarrow{t=\infty} \infty$$

$$n > 1$$

$$\tilde{L} = \frac{\sigma_{appl} \lambda^n h}{\eta_0 L_c} \left(t_{duration}{}^{1-n} \right) \xrightarrow{t=\infty} 0$$

Can a rheometer experiment be characterized by a range of observable $\tilde{L}$? For a given material and duration of experiment, $\tilde{L}$ is bounded by the applied stresses ($T_{min}<T<T_{max}$). Within this range, the duration of the experiment will bound $\tilde{L}$. As explored previously, rheometers do have a resolution limited by a characteristic length scale. The duration of

the experiment should therefore be at least as long as the material would take to move across the resolvable distance. This time is:

$$t_{required} = \frac{\theta_c \eta_{mat}}{2\pi\sigma_{applied}}$$

If we use this time in our $\widetilde{L}$ calculation we find:

$$\widetilde{L} = \frac{\sigma_{appl} \frac{\theta_c \eta_{mat}}{2\pi\sigma_{applied}} h}{\eta_{mat} L_c}$$

$$\widetilde{L} = \frac{\theta_c h}{2\pi L_c}$$

θ_c limits how well a rheometer can evaluate the product $\frac{L_c}{\widetilde{L}h}$. For instance for an application where the L_c is 1µm and the film thickness is 100µm , the AR-G2 could not measure $\widetilde{L}$ smaller than 4.0e-4 (for the duration we calculated above).

Relationship of this number to the Deborah Number

The Deborah number is defined as the ratio of the relaxation time scale to the scale of observation.

$$De = \frac{t_{relaxation}}{t_{observation}}$$

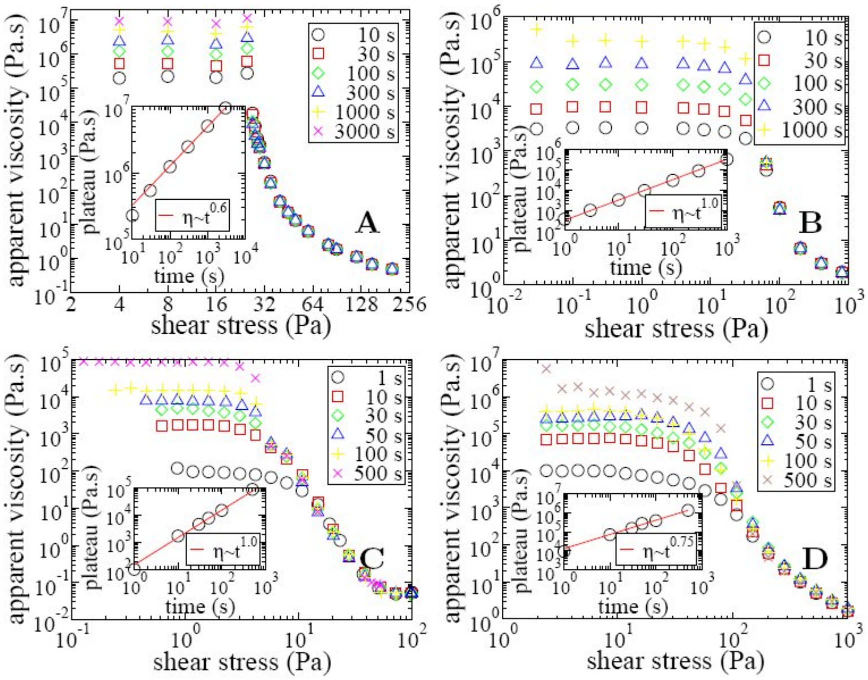
$\widetilde{L}$ is a reformulation of the Deborah Number's inverse.

$$t_{relaxation} = \frac{L_c \eta_{\sigma_{applied}}}{h\sigma_{applied}}$$ and $t_{observation}$ is $t_{duration}$.

The definition of $\widetilde{L}$ attempts to specifically separate out experiment details ($t_{duration}$, L_c, h, $\sigma_{applied}$) from material properties (η), where as the De does not specifically segregate experiment from material.

Remarks on Presentation of Paper

This series of graphs is a classic example of trying to fit too many ideas into a small area. One suggestion is to reposition the legend so that the legend overlaps the north-east corner of each graph to eliminate the unhelpful tick marks in this area. The inset graphs should be removed and perhaps plotted separately as neither axis shares the same units with the larger graph.



Both of these graphs illustrate the authors' points more clearly than the graph below. Here the different stresses are practically indistinguishable from each other. The authors would be wise to relabel the different data series directly on the graph. Also the authors would have done well to focus more on constant stress measurements between 25 and 27 Pa as that is where the Newtonian plateau viscosity develops a time dependence.