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Møller, P.C.F.; Fall, A.; Bonn, D.

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P. C. F. Møller[1(a)], A. Fall[2] and D. Bonn[1,2]

[1] *École Normale Supérieure, Laboratoire de Physique Statistique - Paris, F-75231 France, EU*
[2] *van der Waals-Zeeman Institute, University of Amsterdam - 1018 XE Amsterdam, The Netherlands, EU*

Abstract – For more than 20 years it has been debated if yield stress fluids are solid below the yield stress or actually flow; whether true yield stress fluids exist or not. Advocates of the true yield stress picture have demonstrated that the effective viscosity increases very rapidly as the stress is decreased towards the yield stress. Opponents have shown that this viscosity increase levels off, and that the material behaves as a Newtonian fluid of very high viscosity below the yield stress. In this paper, we demonstrate experimentally (on four different materials, using three different rheometers, five different geometries, and two different measurement methods) that the low-stress Newtonian viscosity is an artifact that arises in non–steady-state experiments. For measurements as long as 10^4 seconds we find that the value of the "Newtonian viscosity" increases indefinitely. This proves that the yield stress exists and marks a sharp transition between flowing states and states where the steady-state viscosity is infinite —a solid!

Introduction. – Yield stress materials can be either "fluid" or "solid"; a typical example is toothpaste, that flows (*i.e.*, is fluid) when pushed out of the tube but no longer flows (is solid) under the influence of gravity while posed on a toothbrush. Such materials are of paramount importance for a large number of applications; examples are concrete, oil drilling fluids, granular and building materials, cosmetic products, and foodstuffs. For all these yield stress fluids, it is important to understand their flow characteristics and notably the yield stress to correctly predict their flow behavior.

The canonical yield stress picture assumes that the material is solid until a critical shear stress is exceeded. Above that stress the material yields and subsequently flows. The Bingham or the Herschel-Bulkley (H-B) models are widely used to describe such behavior; the latter reads: $\sigma = \sigma_y + \alpha\dot{\gamma}^n$, where σ is the shear stress (the subscript y indicates the yield stress) and $\dot{\gamma}$ the velocity gradient or shear rate; a and n are adjustable model parameters. This model can successfully describe the flow behavior of "simple" yield stress fluids such as carbopol, emulsions, foams, etc. over large ranges of shear rates. In *thixotropic* yield stress fluids, the viscosity and yield stress increase with time when the sample is at rest (called aging),

but decrease with time under shear (called rejuvenation). This leads to time-varying viscosity and yield stress, viscosity bifurcation, and other interesting phenomena. (For a recent mini-review see [1].) In this study we have examined only simple yield stress fluids, but we briefly compare our results to measurements on thixotropic yield stress fluids.

For our discussion, the key prediction of the H-B and other simple yield stress models is that the viscosity (defined as the ratio of the stress and shear rate) diverges continuously when the yield stress is approached from above. Hence, below the yield stress, the viscosity is infinite, and the material behaves as a solid. Figure 1A), depicts a H-B fit to the viscosity of a carbopol sample, from which it appears that the viscosity indeed diverges as σ is decreased towards σ_y.

However, for a number of years there has been a controversy as to whether or not the yield stress marks a transition between such a "solid" and a "liquid" state, or if it instead marks a transition between two liquid states with very different viscosities. That is, if true yield stress fluids actually exist. Probably the earliest work that seriously questions the solidity of yield stress fluids below σ_y is a 1985 paper by Barnes and Walters [2]. They show data on carbopol samples apparently demonstrating the existence of a finite viscosity plateau (*i.e.* Newtonian
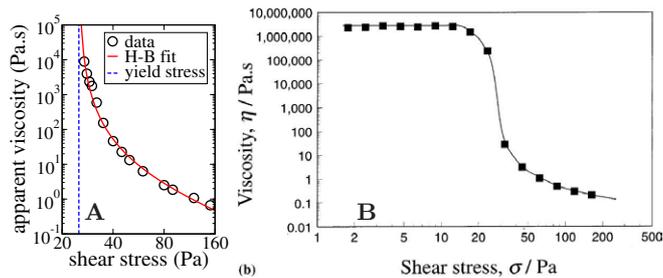
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(a)E-mail: peder.moller@gmail.com

Fig. 1: (Colour on-line) A) The Herschel-Bulkley model provides a good fit to the viscosity of a carbopol sample ($0.2\%_{mass}$ at $pH = 7$) as σ is lowered towards σ_y. B) Measurements on an identical carbopol sample apparently demonstrate the existence of a Newtonian limit below the "yield stress" [3]. This figure is representative of the figures claimed to demonstrate that yield stress materials flow below the yield stress. With kind permission from Elsevier.

behavior) at very low shear stresses —rather than an infinite viscosity below the yield stress. In his review paper on the subject *The yield stress —a review or "παντα ρει"— everything flows?*, Barnes presents numerous curves with viscosity plateaus at low stresses [3]. One of these curves is reproduced in fig. 1B) where the viscosity plateau appears very convincing.

Following these publications, a series of papers appeared discussing the proper definition of yield stress fluids, whether they existed or not, and how to demonstrate either way, *e.g.* [4–8]. The outcome of this debate has been that the rheology and soft matter communities presently hold two coexisting yet conflicting views: 1) the yield stress marks a transition between a liquid state and a solid state, and 2) the yield stress marks a transition between two fluid states that are not fundamentally different —but with very different viscosities.

In this letter, we reproduce the experiments used to demonstrate Newtonian limits below the yield stress and we too find the apparent viscosity plateaus at low stresses. However, we show that such curves are artifacts that arise when falsely concluding that a steady state has been reached. We find that, for imposed stresses below the yield stress and for measurement times at least as long as 10^4 seconds, apparent viscosities increase with time and show no signs of approaching a constant value. This reveals that below the yield stress, the material is not fluid but solid.

In order to experimentally examine the nature of the yield stress transition as well as to test the generality of our findings, we used four different yield stress fluids, three different rheometers, five different measurement geometries and two different measurement protocols. The materials used were; carbopol, a commercial hair gel (Gatsby Water Gloss/Wet Look Soft), a commercial shaving foam (Gillette Foamy Regular), and a cosmetic water-in-oil emulsion. Carbopol is being used on a huge industrial scale as a thickening/yield stress agent but it is also a favorite "model" simple yield stress fluid

for researchers [2,3,9–12]. Carbopol powder consists of small "sponges" of cross-linked polyacrylic acid resins that, under neutral pH swell so enormously in water that concentrations of carbopol even below $0.1\%_{mass}$ are sufficient for the particles to jam together to form a yield stress fluid [9]. The carbopol sample used for the experiments presented here was prepared by mixing 0.2% by mass of carbopol Ultrez U10 grade and ultra-pure water thoroughly for at least an hour which forms an opaque, viscous fluid with no yield stress. The pH is then adjusted to 7 by adding NaOH, leading to a clear material with a yield stress. After pH calibration and thorough mixing, the fluid was left for at least a day and mixed again, before any measurements were done. The commercial hair gel containing carbopol, water and triethanolamine as a stabilizing agent was also mixed prior to use to assure homogeneity. The foam can be shaken well before dispensing the foam, and since the very first and the very last foam from the can differs from the rest, only foam from the bulk was used for the experiments. The water-in-oil emulsion (IB80, Fabre, France) was described previously in [13] and remains stable under shear. The size of the water droplets measured by microscopy was around $7\,\mu$m. For all systems, the characteristic time scales of possible changes in the material properties (such as merging of bubbles and drops in the foam and emulsion —called coarsening) were much larger than the duration of our tests.

The measurements on the carbopol and the hair gel presented here were done using a vane-cup geometry (9 mm inner radius, 13.25 mm outer radius and 52 mm height) in a controlled stress rheometer (Stresstech from Rheologica). The measurements on the foam were made with another vane-cup geometry (11 mm and 14.4 mm radii, and 16 mm height) on a Paar Physica MCR 300 rheometer, while the measurements on the emulsion were done with a cone-plate geometry with a 25 mm radius and a 1° opening angle on the MCR 300. These measurements were double-checked on a Haake RS150 instrument. Besides the measurements shown here we also performed measurements with 12.5 mm radius cone-plate geometries with opening angles of 0.25° and 1°. All geometries had roughened walls in order to prevent wall slip effects during measurements. All results presented here are independent of the rheometer and geometry, indicating that wall slip was successfully prevented [13] (see fig. 5B)). Shear banding in non-thixotropic yield stress fluids (as opposed to thixotropic yield stress fluids) happens only if there is significant stress variation within the geometry. So the fact that our measurements are independent of whether a vane cup (with a large stress variation) or a cone plate (with a negligible stress variation) is used, demonstrates that shear banding does not affect our conclusions (wall slip would affect a thin gap more than a large one).

The main issue is whether the viscosity is finite or infinite below the yield stress. This means resolving very small shear rates which classical rheology does better than velocimetry. We therefore made classical creep tests: the
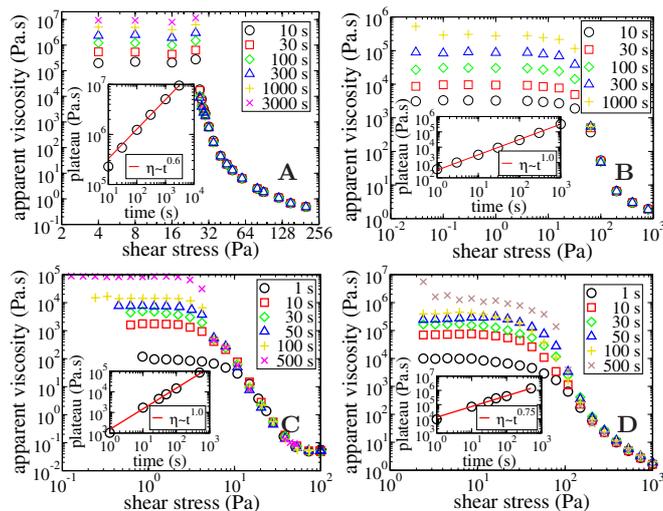
Fig. 2: (Colour on-line) Reproductions of measurements like the one on carbopol in fig. 1A). For each material and each measurement time the resulting curve resembles that in fig. 1A), but the values of the plateaus increase with measurement time. The insets show that the plateaus increase as power laws with time with exponents in the range 0.6–1.0. A) The 0.2% carbopol sample. B) The hair gel. C) The foam. D) The emulsion.

shear stress is imposed and the resulting global shear rate is recorded. We use the term *apparent* viscosity for the stress divided by the instantaneous shear rate to underline that this quantity might be time dependent and hence not a "true" viscosity —even for a constant stress. The resulting apparent viscosity *vs.* shear stress curves are shown in fig. 2. For all samples, low-stress Newtonian viscosity plateaus very similar to the ones reported in the literature are found. However, while the measurements for all measurement times collapse at stresses higher than the "yield stress", the apparent viscosity values are time dependent below it: the viscosity value of the Newtonian viscosity plateau increases with the measurement time. It is clear that, when seen individually, each curve for the four different materials shown in fig. 2 can easily be misleading since such nice plateaus are normally seen only for Newtonian, time-independent materials. In reality, the viscosity value of the 'Newtonian plateau' increases without bound. Although the trend is identical, the four different systems give slightly different exponents for the time evolution of the viscosity: $\eta \sim t^{\mu}$, with $\mu \in [0.6, 1]$, as shown in the insets in fig. 2. This power law behavior shows that the material is not simply a Kelvin-Voigt material (schematically presented as an elastic spring and a viscous damper in parallel), since the apparent viscosity would then have increased exponentially.

It should be underlined that measurements for each material presented here were made on the very same sample. Two different samples from the same batch gave identical results. Near the end of a series of measurements, initial measurement points were reproduced to make sure

that evaporation, aging or material degradation had not changed the properties of the material. After loading the sample into the geometry and between constant, imposed stress measurements, the material is allowed to relax at zero applied stress for half an hour to partially relieve internal stresses built up during loading or during the previous measurement.

To demonstrate the robustness of the phenomenon two different test methods were used. *Method 1* was used on the carbopol and the hair gel sample. Here, a constant stress is imposed and the apparent viscosity is recorded as function of time for each stress. This corresponds to a vertical cut in fig. 2. *Method 2* was used on the foam and emulsion. Here, the imposed stress was increased stepwise, with the duration of each step (over which the apparent viscosity is averaged) varying from series to series. This corresponds to moving along a particular set of symbols in fig. 2. As is evident from fig. 2, independently of the measurement method, material, rheometer, and measurement geometry, we retrieve the apparent plateaus at low stresses, that evolve with time and thus do not correspond to steady-state viscosity values.

We believe that the viscosity plateaus reported in the literature (such as those in [2,3] and references therein) are in general caused by the phenomenon we demonstrate here, and that they are therefore not to be trusted unless data demonstrating that the measurements represent a steady state are provided. We have demonstrated that measurement times much longer than 10000 seconds are needed to reach a steady state for typical yield stress fluids, and we believe that authors would surely have commented on the need for so long measurement times had they been aware of it. For the specific case of carbopol, the data in fig. 1B) agree perfectly with our measurements of carbopol after five minutes of stress in fig. 2A). Five minutes is normally a reasonable time to reach steady state in a rheology experiment, and in combination with the nice Newtonian plateaus, this is perhaps the reason why previous authors have not questioned whether their data corresponded to a true steady state.

In fig. 3 the qualitative difference between imposing a stress below and above the yield stress of the 0.2% carbopol sample is clearly seen. For stresses at or above 27 Pa the viscosity quickly reaches a steady value, but for stresses at or below 25 Pa (corresponding to the last point in the viscosity plateau of 0.2% carbopol) the viscosity keeps increasing in time as $\eta \sim t^{0.6}$ for times even longer than 10^4 seconds. In fig. 4, where the creep compliance (total deformation divided by the imposed stress) is shown as function of time, the difference between the liquid state (with slope 1) above the yield stress and the solid state (with slope zero) below the yield stress is even clearer. Since evidently no steady flow is observed below the yield stress one should not take the instantaneous, apparent viscosity at *any* point in time to be proof of a high-viscosity Newtonian limit at low stresses for these materials.
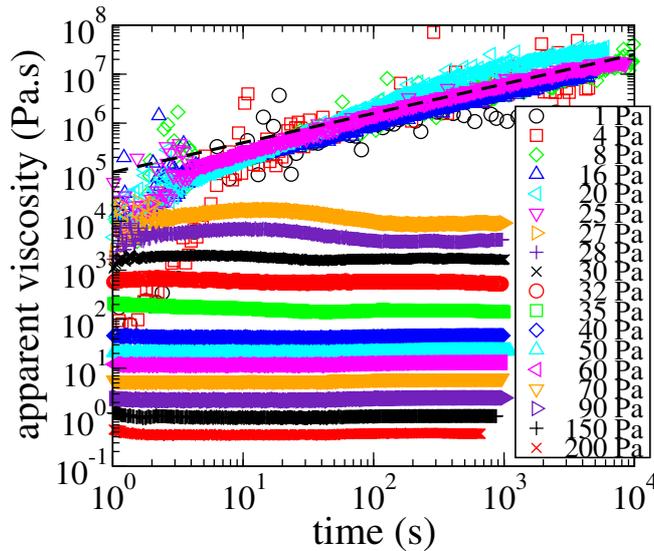
Fig. 3: (Colour on-line) Time evolution of 0.2% carbopol at $p\mathrm{H} = 7$. The apparent viscosity is time independent but stress dependent at 27 Pa and above, but stress independent and increasing with time (close to $\eta \sim t^{0.6}$ as indicated by the dashed line) at 25 Pa and below. This behavior is what gives rise to the stress plateaus.
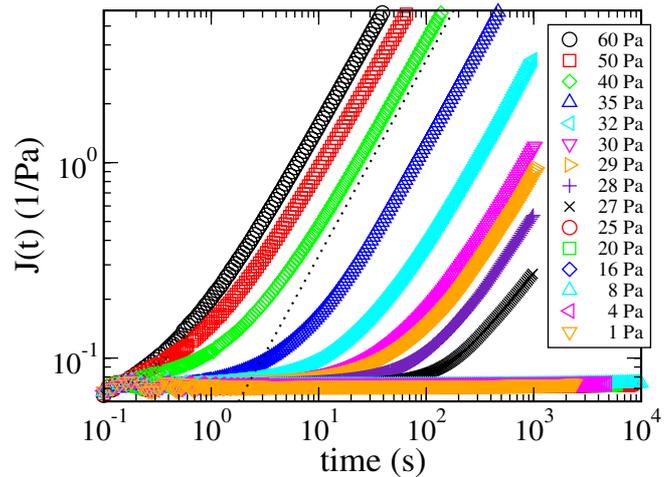

Fig. 4: (Colour on-line) A creep compliance curve of the same data as in fig. 4, showing the time evolution of $J(t)$ —the total deformation divided by the imposed stress. At large t a fluid state will have a slope of 1 (indicated by the dotted line), while a solid state will have a slope of 0. At stresses of 27 Pa and above, slopes are nearly 1, while they are nearly 0 at 25 Pa and below —data for six stresses are collapsed and hardly discernable.

It is interesting to compare our results to similar measurements on *thixotropic* yield stress fluids [14]. The spontaneous aging at rest observed for many soft glassy materials is mostly a thermally driven process, for instance in a colloidal gel where Brownian forces move particles around until they aggregate into a microstructure that resists flow. For glassy systems the thermal noise moves the system through a succession of continuously deeper local minima of the free energy landscape which become continuously harder to escape from [15], implying a higher relaxation time/viscosity. Rejuvenation by the flow can then be looked upon as the shear in the system playing the role of a very high effective temperature, causing the microstructure to break up, or the glassy system to escape from the a local free energy minimum. For such systems it is easy to understand how the materials can age at zero and low stresses; the thermally driven aging of the system is stronger than the shear-induced rejuvenation, and with time the material ages and the viscosity increases. In [16] for example, the authors do creep measurements and for different stresses plot the total strain as function of time. They too find that at long times the total strain saturates for low stresses and progresses linearly for high stresses —indicating that also for thixotropic yield stress fluids the "solid" state is indeed solid. They also find that for stresses below the yield stress the material ages, but this is not surprising since the materials are thixotropic and age at rest. Unfortunately they do no plot the apparent viscosity as function of time so it cannot be seen whether the viscosity is stress independent below the yield stress and would give rise to apparent

viscosity plateaus. If a material is sufficiently thixotropic, the breakdown of viscosity with increasing shear rates is so significant that not only the steady-state viscosity but also the steady-state shear stress $(\sigma_{ss}(\dot{\gamma}) = \dot{\gamma} \cdot \eta_{ss}(\dot{\gamma}))$ becomes a decreasing function of the shear rate in some region —there is a local minimum in $\sigma_{ss}(\dot{\gamma})$. When decreasing the shear stress below this minimum, the steady-state shear rate of the material changes abruptly from the critical shear rate (corresponding to the minimum of $\sigma_{ss}(\dot{\gamma})$) to zero. Since the viscosity changes discontinuously from a finite value to infinity this is called "viscosity bifurcation" [17]. Such viscosity bifurcation in thixotropic yield stress fluids is seen in viscosity *vs.* time curves in for instance [17] and [18], where the jump between the apparent viscosities of the liquid states and the solid states is *much* bigger than in fig. 3. In those figures the stress variation is unfortunately too little to show whether the viscosity is stress independent and would show apparent viscosity plateaus. If not the shear stress, but the shear rate is imposed on a thixotropic yield stress fluid it is possible to obtain an *average* shear rate below the critical shear rate. But in this case the fluid will separate into two phases. One solid and one being sheared at the critical shear rate —in a ratio so that the average shear rate is equal to the one imposed. In stark contrast to shear banding in simple yield stress fluids, this low-rate–induced shear banding happens even if the shear stress is identical in the two phases [19]. For a recent review of shear banding in thixotropic yield stress fluids, see [20].

To verify that our materials were *not* thixotropic (which would trivially explain the aging at low shear stresses)
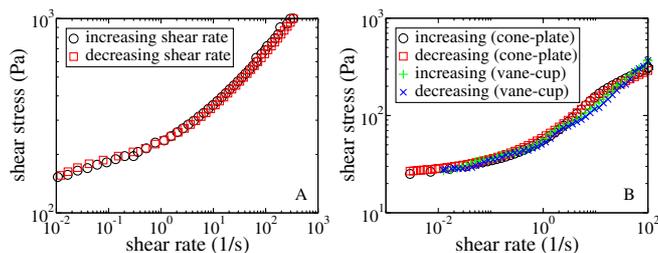
Fig. 5: (Colour on-line) A material is normally tested for thixotropy by imposing an up-down rate sweep, where the shear stress is measured while the shear rate is progressively increased and then decreased. If the material is thixotropic, the viscosity is time dependent leading to a hysteresis effect: the increasing and decreasing curves do not overlap. Both the emulsion (A), and the carbopol (B) are seen to be entirely non-thixotropic, as is the also case for the foam and the hair gel (data not shown). Carbopol data from measurements with both the 25 mm radius cone-plate geometry and the 14.4 mm radius vane-cup geometry collapse nicely, demonstrating that consistent results are obtained even with completely different geometries. Since wall slip would have caused two geometries with very different gap sizes to yield different results at low shear rates, this collapse for data from geometries with 0.2 mm and 3.4 mm gaps respectively demonstrates that we avoid wall slip.

we measured their response to up-down stress sweeps and confirmed that the "up" and "down" curves overlap (fig. 5). This is a standard way of measuring thixotropy since had the material been thixotropic, the flow at high stresses would have broken down the structure resulting in a lower viscosity and yield stress in the "down" sweep than in the "up" sweep.

The question is therefore how to understand this "aging under stress" of a non-thixotropic system? The absence of aging at rest is easy to understand. For the systems used here, the thermal agitation is not nearly enough to reorganize the arrangement of droplets, bubbles, or carbopol "sponges", since due to the large size of the particles or bubbles, the free energy barriers for structural reorganization are much larger than kT. This is why in the experiments, there is no detectable aging of these systems when they are at rest. However, if a stress is imposed on the material the energy landscape is tilted, facilitating reorganizations in the direction of the imposed stress. If the imposed stress is so large that the system can escape from all of its local minima, the material will keep flowing at this stress and a "simple" viscous flow results. However, if the imposed stress is large enough to cause some structural reorganization but insufficient for the system to explore all of the available phase space, the system will age just as described above for the thixotropic systems, the imposed stress playing the role of an increased effective temperature. This is very similar to a loose granular material that does not compact (age) when left at rest, but does when subject to small shear rates or vibrations. That small stresses can actually facilitate

aging processes rather than rejuvenation processes has previously been observed for some thixotropic systems and has been termed "overaging" [21–23]. It has until now not been observed in non-thixotropic materials.

In conclusion we have shown that the many viscosity *vs.* stress curves in the literature showing Newtonian limits at low stresses should not be trusted unless data proving that the points represent a steady state are provided. This is because, below the yield stress, the viscosity is independent of stress but increases as a power law in time after the stress has been imposed, so that recording the viscosity after say 100 seconds will give one viscosity plateau while data at 1000 seconds will give another. So the instantaneously measured viscosity does not represent a steady state and should not be reported as a proof for a Newtonian limit for the material at low stresses. We have demonstrated this increase of the viscosity with time for four different typical simple yield stress systems and it persists for at least as long as 10000 seconds. Our findings are well explained qualitatively by assuming that aging of the system happens at experimental time scales only if a small but non-zero stress is applied to the system: at zero stress the thermal agitations are too weak to cause reorganizations, and at too high stress the material constantly flows and the system is rejuvenated. The yield stress is the limit between "aging stresses" and "rejuvenation stresses": above it the material flows with a time-independent viscosity, and below it the system ages and the steady-state viscosity is infinite. Thus, the yield stress is real, and it marks a transition between a flowing and a "solid" state.

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