Rheology in the Teaching Lab: Properties of Starch Suspensions

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Abstract

In everyday life we encounter many complex fluids, from shear-thinning paint and toothpaste to shear-thickening starch suspensions. The study of their properties offers an opportunity for students to relate sophisticated physical concepts to their everyday experience. Modern rheology uses expensive equipment impractical for the teaching laboratory. Here we describe a rudimentary rheometer suitable for student laboratories that can demonstrate and quantify discontinuous shear thickening, the most dramatic property of complex fluids, and use it to measure the properties of starch suspensions.

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I. INTRODUCTION

Simple fluids, such as water, honey, oils, pitch and liquid nitrogen have the “Newtonian” property that their stress is proportional to their strain rate (flow rate). Their ratio is a scalar viscosity\(^1\). This proportionality defines a simple fluid, whatever the value of the viscosity.

In contrast, there are “non-Newtonian” fluids with more complicated relations between stress and strain rate. These fluids may contain polymers, or be suspensions (typically in a Newtonian solvent) of solid particles, membrane-bound vesicles or droplets of an immiscible fluid (emulsions).

Paint, ketchup, toothpaste and corn starch suspensions are familiar examples of non-Newtonian fluids. Most of these are shear-thinning: they may have a small finite strength at rest (which is why toothpaste doesn’t flow out of its tube unless squeezed, or ketchup out of its bottle, unless squeezed, shaken or struck) or a viscosity that decreases as the flow rate is increased (so that paint is easily spread with a brush, but doesn’t drip once spread). Unlike these, starch suspensions have the remarkable property, known to schoolchildren who gave them the nickname “oobleck” after a fictional substance, of suddenly turning stiff, increasing their viscosity by orders of magnitude, if the strain rate exceeds a threshold. Brown and Jaeger \[^{1}\] provide a recent review of the properties of these suspensions.

A student laboratory experiment will excite more interest if it is novel, if it explores a dramatic phenomenon, and if it is related to students’ everyday experience. The “discontinuous” (abrupt) shear stiffening of starch suspensions meets these criteria. Yet quantitative rheometry requires expensive and delicate equipment unavailable in and unsuitable for the student laboratory. Here we describe, and report on results obtained with, a rudimentary rheometer that can be assembled from a few dollars’ worth of equipment. With the aid of a consumer-grade video camera, it can produce quantitative data.

\[^{1}\] This discussion is limited to essentially incompressible fluids, usually an excellent approximation. When compressibility is important, as for sound waves, an additional scalar bulk viscosity must be defined.
II. THE INSTRUMENT

The instrument is shown, approximately to scale, in Fig. 1. A light-emitting diode mounted on the top of the rod was used to determine the position of the rod against an aligned meter stick with an attached LED that serves as a reference. Data were recorded with a video camera at one or 30 frames per second (the lower recording rate was used for more slowly sinking rods because of limited camera memory), and the velocity averaged over 20 frames if recorded at 30 fps and over 5 frames if recorded at 1 fps. Averaging was necessary because the rod position was determined to only ±0.5 line in the video image, or about ±0.1 mm; accuracy was limited by the resolution of the video image. Data were processed with ImageJ software [2]. The rods were 36 cm long, rounded to a hemisphere at their lower ends, with diameters 18.9 mm. The guide sleeve had an internal diameter of 19.8 mm and was 12.5 cm long. The cylinder (a nominal 50 ml graduated cylinder but with larger total volume) had an internal diameter of 23.5 mm and depth, rim to interior bottom, of 16.5 cm. The aluminum rod had a mass of 271 g and the stainless steel rod a mass of 820 g.

III. THEORY

A. Newtonian Fluids

We make the approximation that the annulus, of uniform width \( h \) (if the rod is perfectly centered in the cylinder) is thin compared to the radius \( r \) of the rod. Then the geometry of the annulus may be approximated as that of a planar duct. The full theory [3] of the flow in a cylindrical annular duct in which the inner wall is moving with respect to the outer wall is cumbersome, and its use would not be justified in these experiments in which the geometry cannot be controlled precisely and the two cylinders may not be accurately coaxial. If \( h \ll r \) the rod sinks much more slowly that the fluid flows, so that the solution for flow in a planar duct with stationary walls may be used. Because the gap is everywhere narrow compared to \( r \) the case of an off-center rod is also readily dealt with.

For a Newtonian fluid with single-valued dynamic viscosity \( \eta \) and a pressure gradient \( \frac{d\rho}{dz} \)
FIG. 1: The rudimentary rheometer consists of a cylinder filled with the fluid whose properties are to be measured. A metal rod with diameter slightly less than that of the cylinder sinks into the fluid, driving fluid up the annulus between rod and cylinder. The rod is guided and centered in the cylinder by a cylindrical sleeve aligned with the cylinder axis.

Parallel to the duct walls the fluid velocity

\[ v(y) = \frac{1}{2\eta} \frac{dp}{dz} \left( y^2 - \frac{h^2}{4} \right), \]  

(1)

where \( y \) is the transverse coordinate in the duct with \( y = 0 \) at its midplane. If the rod is centered in the cylinder the fluid flow rate per unit circumference

\[ \dot{q} = \int_{-h/2}^{h/2} v(y) \, dy = -\frac{h^3}{12\eta} \frac{dp}{dz}, \]  

(2)

and the total fluid flow rate \( \dot{Q} = 2\pi r \dot{q} \). The rod sinks at a rate

\[ v_{rod} = \frac{\dot{Q}}{\pi r^2} = \frac{h^3}{6\eta r} \frac{dp}{dz}. \]  

(3)
The ratio of \( v_{rod} \) to the fluid velocity at \( y = 0 \)

\[
\left| \frac{v_{rod}}{v(0)} \right| = \frac{4}{3} \frac{h}{r} \ll 1,
\]

justifying the use of the solution Eq. 1 for flow in a duct with stationary walls.

The pressure gradient in the flowing fluid is given by the weight per unit cross-sectional area of the rod, allowing for the buoyancy of the displaced fluid, divided by its immersed length \( z_r \):

\[
\frac{dp}{dz} = g \left( \frac{\rho L - \rho_f z_r}{z_r} \right),
\]

where \( \rho \) is the density of the rod (2.7 g/cm\(^3\) for aluminum, 8.0 gm/cm\(^3\) for stainless steel) and \( \rho_f \) is the density of the fluid. The buoyancy correction \( \rho_f z_r \) is small if the immersed length is small compared to the rod length, as it will always be when the rod has just entered the fluid, and is never more than about 20\% in our experiments.

In order to obtain a simple analytic result we neglect buoyancy. The equation of motion of the rod (inertia is negligible for a viscous fluid) is

\[
\frac{dz_r}{dt} = v_{rod} = \frac{h^3 \rho \rho L}{6 \eta r z_r}
\]

with the elementary solution

\[
v_{rod} = \sqrt{\frac{h^3 \rho \rho L}{12 \eta r}} t^{-1/2}.
\]

Although we use a guide tube to try to keep the sinking rod as close and parallel to the axis of the fluid-filled cylinder as possible, alignment is not perfect and we consider the effects of its being off-center. If the axis of the rod is displaced from the axis of the cylinder by \( \Delta x \) the width of the gap between rod and cylinder, to lowest order in the small quantity \( \Delta x/r (\Delta x \leq h) \), is

\[
\Delta r(\theta) \approx h - \Delta x \cos \theta,
\]

where \( \theta \) is the angle from the direction of \( \Delta x \). Then

\[
\dot{Q} = \int_0^{2\pi} d\theta r \dot{q}(\theta) = -\frac{\pi r h^3}{6 \eta} \frac{dp}{dz} \left[ 1 + \frac{3}{2} \left( \frac{\Delta x}{h} \right)^2 \right].
\]
For an off-center rod $\dot{Q}$ and $v_{rod} = \dot{Q}/\pi r^2$ can be as much as $5/2$ times greater than for a centered rod (in the $h \ll r$ approximation). We have ignored the fact that if the rod is very close ($\Delta r(\theta) \lesssim h\sqrt{h/r}$) to the cylinder wall the approximation Eq. 3 is not valid and additional drag is contributed by the relative motion of rod and wall.

### B. Shear stiffening fluids

In a shear stiffening fluid the viscosity is an increasing function of the strain rate. The behavior of such fluids is complex, but often may be approximated by the condition that the viscosity increases abruptly by orders of magnitude if the strain rate $|\dot{\gamma}| > \dot{\gamma}_c$, where $\dot{\gamma}_c$ is a critical strain rate \[1\]. As a result, Eq. 1 breaks down if it implies $|\dot{\gamma}| = \frac{1}{\eta} |\frac{dp}{dz}| y > \dot{\gamma}_c$, where $\eta$ is the viscosity in the unstiffened regime. The value of $\dot{\gamma}_c$ is generally taken as an empirical parameter, but has been explained as the result of surface tension \[4\].

If Eq. 1 implies $|\dot{\gamma}| > \dot{\gamma}_c$ the suspension undergoes discontinuous shear thickening in the outside of the duct, where $|y| > \gamma_c\eta/|\frac{dp}{dz}|$. This stiffening, increasing $\eta$ by orders of magnitude under conditions in which $\eta\frac{d^2u}{dy^2} = \frac{dp}{dz}$ is continuous across the duct, implies $\frac{dv}{dy} \to \text{Constant}$, except for a central region in which $|y| < \gamma_c\eta/|\frac{dp}{dz}|$ and Eq. 1 applies. However, in the limit $h/r \to 0$ the difference in velocity of the duct walls $|v_{rod}| \to 0$ (because $|v_{rod}/v(y)| = \mathcal{O}(h/r)$; Eq. 4) so that the condition that the fluid velocity at a duct wall equal the wall velocity implies Constant $\to 0$ and $\dot{\gamma} \to 0$. The continuity of stress across the duct implies an additional factor of the large shear thickened $\eta$ in the denominator of $\dot{\gamma} = dv/dy$ (Eq. 1). This shear-thickened solution is not self-consistent: shear thickening reduces the strain rate below the shear-thickening threshold.

A self-consistent solution is found if $|\dot{\gamma}|$ remains at the shear thickening threshold $\dot{\gamma}_c$ across the duct, aside from the central region \[5\]. Then, assuming this central region is negligibly thin,

$$\dot{q} = \dot{\gamma}_c \frac{h^2}{4},$$ \hspace{1cm} \text{(10)}$$

$$\dot{Q} = \dot{\gamma}_c \frac{\pi rh^2}{2},$$ \hspace{1cm} \text{(11)}$$

and

$$v_{rod} = \frac{\dot{Q}}{\pi r^2} = \dot{\gamma}_c \frac{h^2}{2r}.$$ \hspace{1cm} \text{(12)}
FIG. 2: Sinking rate \( v_{rod} \) of aluminum and stainless steel rods in viscous cane sugar solution. From the measured sink rate and Eq. 7, the viscosity \( \eta \approx 0.7 \text{ Pa-s} \) and the Reynolds number \( \text{Re} \approx 0.1 \) for the Al rod and \( \text{Re} \approx 0.3 \) for the steel rod at \( t = 1 \text{ s} \). The data sampling rate was 30/s, but the points shown represent boxcar averages of 20 points, taken to smooth otherwise noisy data.

The sink rate is predicted to be independent of the weight of the rod. It depends on the nature of the suspension through the empirical \( \dot{\gamma}_c \) (Chu, et al. [4] have suggested \( \dot{\gamma}_c \) depends on surface interactions and the width of the duct, but this has not been demonstrated).

For an off-center rod the result Eq. 9 is replaced by

\[
\dot{Q} = \int_0^{2\pi} d\theta r \dot{q}(\theta) = \dot{\gamma}_c \frac{\pi rh^2}{2} \left[ 1 + \frac{1}{2} \left( \frac{\Delta x}{h} \right)^2 \right].
\]  

(13)

Then \( \dot{Q} \) and \( v_{rod} = \dot{Q}/\pi r^2 \) can be as much as 3/2 times greater than for a centered rod (in the \( h \ll r \) approximation).

IV. RESULTS

As a test of the method and apparatus, we first used a viscous solution of cane sugar in water. The results are shown in Fig. 2. The proportionality \( v_{rod} \propto t^{-1/2} \) for time \( t \) after the rod enters the solution agrees with the prediction Eq. 7 for a Newtonian fluid. The neglect of inertia in Eq. 6 is justified by the self-consistent result that the Reynolds number \( \text{Re} = hv_{rod}/\eta \ll 1 \) throughout the run (Re \( \approx 0.1 \) for the Al rod at \( t = 1 \text{ s} \)).

The sinking rates of aluminum and stainless steel rods in suspensions of corn, potato and tapioca starches in isopycnic (density matched) CsCl brines are shown in Figs. 3–5. All suspensions had starch volume and mass fractions of 43%, well into the regime in which
FIG. 3: Sink rates of aluminum and steel rods in a 43% suspension of corn starch. Data were sampled every second, but each point shown is a boxcar average over five seconds.

FIG. 4: Sink rates of aluminum and steel rods in a 43% suspension of potato starch. The data sampling rate was 30/s, but the points shown are boxcar averages over 20 samples.

discontinuous shear thickening occurs, but a low enough concentration that the suspensions are shear thinning fluids (rather than pastes with finite strength) at low strain rates.

The results for the starch suspensions are mixed. In corn starch (Fig. 3) the steel rod sank at a nearly constant rate, as expected (Eq. 12) for a shear thickened suspension. The implied stiffening threshold $\dot{\gamma}_c \approx 4$/s, typical of previous measurements of corn starch suspensions [1, 4, 6] (that are widely scattered, perhaps as a result of differing properties of this poorly standardized natural product). The varying sink rate of the aluminum rod might be attributed to a varying displacement from a centered position in the cylinder (Eq. 13). The greater stability of the sink rate of the steel rod was observed in two other pairs of runs (not shown).
FIG. 5: Sink rates of aluminum and steel rods in a 43% suspension of tapioca starch. The data were sampled at a rate of 30/s, but each point shown is a boxcar average over 20 samples.

The generally increasing sink rates of potato starch suspensions may be attributed to motion of the rods from centered to off-center positions in the cylinder, and the initial decrease may be the result of a transient phase in which the suspension is unstiffened, as expected and found for a Newtonian fluid shown in Fig. 2. The steel rod sank about 50% faster than the aluminum rod through most of its descent, although towards the end the aluminum rod speeded up to a sink rate as fast as the maximum sink rate of the steel rod. The inferred $\dot{\gamma}_c \approx 20-30$/s.

The tapioca starch suspensions are close to the predictions of Eq. [12]. The sink rates were roughly constant after an initial increase by a factor of 1.5, consistent with motion of the rods from centered to near-wall positions (Eq. [13]), and were nearly independent of the weight of the rod. The implied $\dot{\gamma}_c \approx 40$/s.

Qualitatively, the results for starch suspensions followed predictions: the sink rates were roughly independent of the rod weight, in contrast to a Newtonian fluid in which the sink rate would be proportional to the rod mass, allowing for buoyancy, which is at least three times greater for steel.

The results are summarized in the Table. There is no apparent correlation between the critical strain rates for discontinuous shear stiffening and the size of the starch grains.
| starch     | grain diameter | $\dot{\gamma}_c$ | CsCl fraction |
|------------|----------------|-------------------|---------------|
| corn       | 14µ            | 4/s               | 52.5%         |
| tapioca    | 14µ            | 40/s              | 52.5%         |
| potato     | 35µ            | 20–30/s           | 54.5%         |

TABLE I: Critical strain rates $\dot{\gamma}_c$ for suspensions of three starches in CsCl brine. Mean grain diameters from Ref. [7]. The mass fractions of CsCl in an isopycnic brine, used to prevent sedimentation, are also shown; we found slightly different densities for the different starches, but these values may be different for different samples of these natural products.

V. DISCUSSION

We have demonstrated a simple rheometer that can be built, or used, by students in an advanced laboratory course at negligible expense and without requiring special facilities. This rheometer can demonstrate basic but unfamiliar properties of Newtonian fluid flow as well as obtaining significant novel data about the properties of complex fluids. It is suitable both as a teaching tool in a curriculum that includes hydrodynamics or rheology and as an introduction to research that produces non-trivial results without the use of expensive state-of-the-art apparatus.

Acknowledgments

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[1] E. Brown and H. M. Jaeger, Rep. Prog. Phys. 77, 046602 (2014).
[2] http://imagej.nih.gov/ij/ accessed June 3, 2014.
[3] W. Müller, Zeit. angew. Math. Mech. 16, 227 (1936).
[4] C. Chu, et al., Phys. Rev. E submitted (arXiv:1405.7233) (2014).
[5] H. M. Laun, R. Bung and F. Schmidt, J. Rheol. 35(6), 999 (1991).
[6] A. Fall, H. Huang, F. Bertrand, G. Ovarlez and D. Bonn, Phys. Rev. Lett. 100, 018301 (2008).
[7] E. M. Snyder, Industrial Microscopy of Starches, in Starch: Chemistry and Technology, eds. R. L. Whistler, J. N. BeMiller and E. F. Paschall (Academic Press, Orlando, 1984).