Gravity flow instability of viscoplastic materials: The ketchup drip

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In contrast with simple liquids such as water, milk, honey, which easily flow as a continuous jet when poured from a vessel, pasty materials such as mayonnaise, mustard, ketchup, puree, etc., fall by fits and starts in a wide range of flow rates. This may, for example, be observed when ketchup or mayonnaise is pushed from a tube at a sufficient height over a plate: although surface tension effects are generally negligible because of its high viscosity the material drops as successive droplets of more or less similar size (except at large flow rates). Here we demonstrate that this effect is a kind of flow instability which develops when the weight of material becomes larger than a force due to its yield stress, namely a critical stress below which it cannot flow steadily. Furthermore, we show that depending on the exact material behavior surprising phenomena may be observed: the size of the droplet may remain constant or even decrease (for thixotropic materials) as the flow rate increases. This approach, for example, provides tools for controlling the shape of droplets in cooking and the size of extrudates in food and mineral industries.

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I. INTRODUCTION

Not too far from the exit a simple liquid jet is continuous if the flow rate is not too small, otherwise surface tension effects induces the formation of approximately spherical droplets which fall when their weight becomes sufficiently large. Moreover, even when it is initially continuous the Rayleigh-Plateau instability [1] occurs beyond a certain distance of flow, which tends to separate the jet in a succession of droplets. For a pasty material, i.e., exhibiting a yield stress τ_c below which it behaves as a solid, our common experience shows that when pouring it at a low flow rate from a vessel an instability takes place: the material advances by fits and starts, even when surface tension effects are far negligible ($\sigma/R \ll \tau_c$, in which σ is the interfacial tension between the paste and the ambient gas, and R the typical radius of the droplet). Surprisingly, although polymer extrusion was the subject of a large number of studies [2,3], as far as we know there has been almost no study concerning the flow characteristics of viscoplastic materials and existing data mainly concern the surface aspect of extrudates [4]. In order to find out the origin of this phenomenon here we consider a situation for which the flow characteristics are controlled, so that we can analyze the data from a simple theoretical approach. We study the flow of various pastes at the exit of a cylinder through which the pastes are pushed. We show that the length of resulting droplets generally increases with the flow rate. We demonstrate that for simple yield stress fluids this effect is a kind of flow instability which develops when the weight of material becomes larger than a force due to its yield stress. Furthermore, we show that depending on the exact material behavior surprising phenomena may be observed: the size of the droplet may remain constant or even decrease (for thixotropic materials) as the flow rate increases.

II. EXPERIMENTS

A. Experimental setup, materials, and procedures

We focused on the flow induced by pushing the paste from a syringe (diameter 6 cm) at a given flow rate through a glass conduit of radius $R_0=3$ mm. We used for that a controlled rate medical pump (Sage M362, *Prolabo*). It is worth noting that although with simple (Newtonian) liquids the rate could be controlled rather precisely, with pastes, the flow rate, which could, nevertheless, remain fixed, was generally different (sometimes significantly) from that expected from the apparatus calibration. As a consequence we determined the effective flow rate by measuring the mass of dropped material in time. For these experiments we used a concentrated emulsion (mayonnaise, *Amora*, $\rho=915$ kg m^{-3}), an organic suspension (ketchup, *Heinz*, $\rho=1130$ kg m^{-3}), a gel (hair gel, *Vivelle Dop*, $\rho=950$ kg m^{-3}), and a mineral suspension (water-bentonite suspension, *Impersol, Sud-Chemie*, solid volume fraction: 9%, $\rho=1150$ kg m^{-3}). The room temperature was maintained close to 20 °C with an air-conditioned system. Due to the relatively slow flows considered here the sample temperature was analogous. The different materials were agitated by hand then set up in the syringe, the tests starting just after this operation. For the tests with the bentonite suspension, the state of which continuously evolves as a result of a strong time-dependent viscosity, we added a diaphragm of 0.5 mm thickness 1 cm before the conduit exit in order to preshear at best the material and set in a given state before the exit for different flow rates. In fact, this procedure did not affect the qualitative trends of our results but mainly damped the sensitivity of data to the exact flow history of the whole material in the syringe. For all materials we increased the flow rate step by step and waited for apparent steady state at each level.

In order to determine the rheological behavior of the material independently we carried out rheometrical tests. We used for that a Bohlin C/VOR controlled stress rheometer equipped with a parallel disk geometry (disk diameter: 30 mm; gap: 1 mm). The disks were roughened (striated, roughness of 0.5 mm) in order to avoid possible wall slip effects. After setting up the material between the disks, a progressively increasing stress was applied up to a fixed value then the stress was decreased to zero. The duration of each of the increasing and decreasing ramps was 1 min.

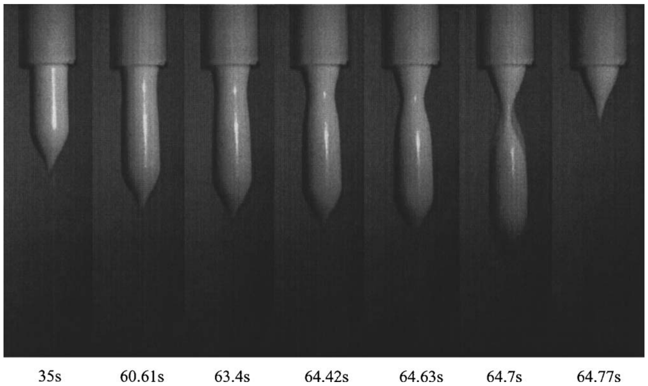

FIG. 1. Successive views of a mayonnaise sample at different times during extrusion at a rate $\nu=2.8$. The initial time (0 s) corresponds to the separation of the previous extrudate.

B. Results

Let us examine the results of our extrusion tests. In a first stage, as it is pushed outside, the material takes a cylindrical shape (except at its bottom because of the deformation undergone during the previous droplet separation) (see Fig. 1). This cylindrical aspect confirms that surface tension effects are negligible at this stage. Then the cylinder diameter starts to decrease in time in some region. The corresponding rate of decrease rapidly increases as the local diameter decreases so that the sample almost instantaneously separates into two parts and a droplet falls (see Fig. 1). The length of this droplet increases with the apparent yield stress of the material. Beyond a critical flow rate (Q_c) the droplets remain in contact over a long distance of fall so that it becomes difficult to estimate their specific weight. In that case the jet resembles a string of sausages, which shows that the instability described above goes on playing a fundamental role. Here we analyze data corresponding to flow rates below Q_c. The droplet weight for a given flow rate (either under the increasing or decreasing ramp) appears to fluctuate from about 3% for the gel to 15% for the ketchup. These fluctuations might be due either to thixotropy effects or slight imperfections of the free surface of the sample. For each flow rate we recorded the average volume of the droplets over five to ten droplets and represented it in terms of the length of separation $X_0=\Omega/\pi R_0^2$, in which Ω is the droplet volume as a function of the flow rate (see Fig. 2). Three behavior types appear: (i) for the gel X_0 progressively increases with the flow rate; (ii) for the ketchup and the mayonnaise X_0 remains almost constant over a wide range of flow rates and seems to start to increase at large flow rates; (iii) for the bentonite suspension X_0 decreases as the flow rate increases.

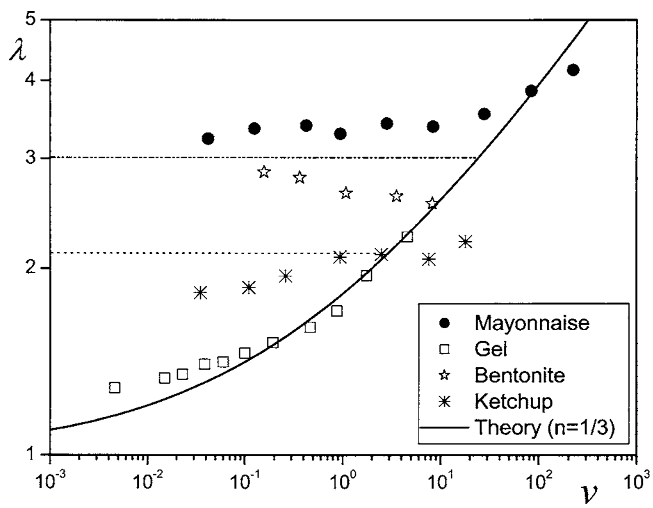

FIG. 2. Dimensionless length of separation ($\lambda=X_0/X_c$) as a function of the dimensionless flow rate (ν) for the different materials (see definitions in text). Here we used rheological parameters as deduced from the Herschel-Bulkley model fitted to the decreasing curve in the rheogram, i.e., (gel) $\tau_{c_1}=51$ Pa, $K=42$ Pa s^n, $n=0.355$; (mayonnaise) $\tau_{c_1}=15$ Pa, $K=29$ Pa s^n, $n=0.333$; (ketchup) $\tau_{c_1}=30$ Pa, $K=21.9$ Pa s^n, $n=0.242$; (bentonite) $\tau_{c_1}=84$ Pa, $K=106$ Pa s^n, $n=0.5$. The theoretical curve [Eq. (2)] does not change significantly for n ranging from 0.33 to 0.355. The curve for $n=0.242$ only slightly departs from this curve. The values of the apparent yield stress for flow start were as follows: (mayonnaise) $\tau_{c_2}\approx 45$ Pa; (ketchup) $\tau_{c_2}\approx 64$ Pa; (bentonite) $\tau_{c_2}\approx 187.5$ Pa ($t_{\mathrm{rest}}=10$ s), $\tau_{c_2}\approx 195$ Pa ($t_{\mathrm{rest}}=60$ s), $\tau_{c_2}\approx 212$ Pa ($t_{\mathrm{rest}}=180$ s), $\tau_{c_2}\approx 230$ Pa ($t_{\mathrm{rest}}=540$ s). The dotted and dash dotted lines indicate the levels of the theoretical λ_c values, respectively, for ketchup and mayonnaise.

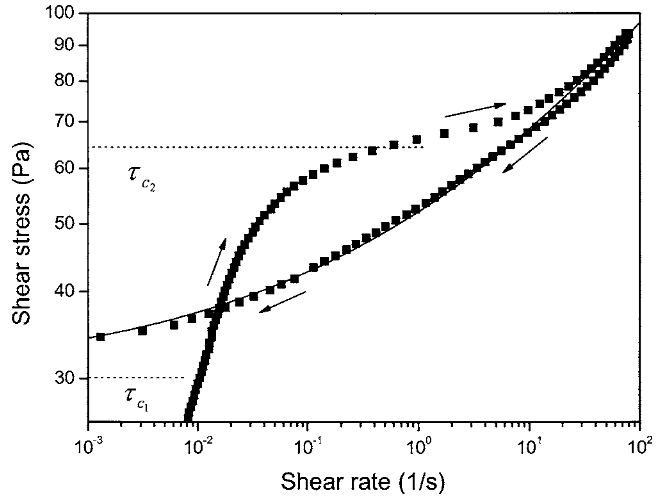

FIG. 3. Typical flow curve of pasty materials (here ketchup) as obtained from an increasing-decreasing stress ramp. The continuous line corresponds to the Herschel-Bulkley model fitted to the decreasing flow curve.

From rheometrical data it appears that our pasty materials effectively exhibit the behavior type described in the next section (see Fig. 3): during an increasing shear stress ramp the material starts to flow in its solid regime, which explains the initial part of flow curve with a steep slope; beyond a critical stress the material reaches its liquid regime; then the decreasing curve takes place in the liquid regime, and this flow curve can be well represented by a Herschel-Bulkley model (see Sec. III) (cf. Fig. 3). However, except for the gel the decreasing curve does not superimpose the increasing curve, there is an hysteresis which indicates that some significant thixotropy effect occurs: the apparent yield stress for flow start (τ_{c1}) differs from the apparent yield stress (τ_{c2}) for stoppage.

III. THEORY

A. Constitutive equation of pasty materials

The basic characteristics of pasty materials is that they undergo a solid-liquid transition under critical conditions (of stress or strain). Assuming that they are perfectly rigid in their solid regime a simple representation of this behavior is of the type

$$\sqrt{-T_{II}} < \tau_c \Rightarrow \mathbf{D} = \mathbf{0} \text{ (solid regime)},$$

$$\sqrt{-T_{II}} > \tau_c \Rightarrow \mathbf{\Sigma} = -p\mathbf{I} + \mathbf{T} = -p\mathbf{I} + F(D_{II})\mathbf{D} + \tau_c \mathbf{D}/\sqrt{-D_{II}} \text{ (liquid regime)},$$

in which $\mathbf{D}$ and $\mathbf{\Sigma}$ are, respectively, the strain rate (symmetric part of the velocity gradient tensor) and stress tensors, p is the pressure, $\mathbf{I}$ is the unit tensor, $\mathbf{T}$ is the extra-stress tensor, $T_{II}=-\mathrm{tr}(\mathbf{T})^2/2$ and $D_{II}=-\mathrm{tr}\,\mathbf{D}^2/2$ the second invariants of the stress and strain rate tensors, and F is a function such that $F(D_{II})D_{II} \to 0$ when $D_{II} \to 0$. Usually the Herschel-Bulkley expression for F $[F(D_{II})=2^n K/(\sqrt{-D_{II}})^{1-n}$, in which K and n are two material parameters$]$ makes it possible to well represent steady-state data. In simple shear conditions for example prevailing in parallel disk flows the constitutive equation expresses in the form of a simple relation between the shear stress (τ) and the shear rate ($\dot{\gamma}=du/dy$, in which u is the tangential velocity and y the vertical position): $\tau=\tau_c + K\dot{\gamma}^n$.

It is worth noting that the above model intends to reflect at best the most important rheological trends of such materials, namely the solid-liquid transition around a critical stress, but it does not account for more complex trends such as possible thixotropy (viscosity increase at rest and viscosity decrease in time under constant shear) or normal stress effects. Thixotropy was often reported for such materials [6] but normal stresses have been observed mainly with concentrated suspensions of noncolloidal particles [7] and it is likely that they in general do not play a significant role in paste extrusion. In the following we discuss the flow characteristics assuming a simple Herschel-Bulkley behavior for each fluid, then we take into account the discrepancy of data from this model.

B. Flow characteristics during extrusion

Let us consider the flow of the extrudate out of the conduit. For the sake of simplicity we assume that its length is much larger than its diameter. Under these conditions it may be demonstrated [5,8] that the paste either remains undeformed or undergoes an elongational flow with the following expressions for the radial and longitudinal velocity components: $v_r=-rd/2$; $v_z=zd$, in which $d=-2\dot{R}/R$ is the rate at which the fluid is strained. Now we can compute $\sqrt{-D_{II}}$ which is found to be equal to $\sqrt{3}|d|/2$. From the above constitutive equation we find that the normal stress may be written as $\tau_{zz}=\varepsilon(2\tau_c/\sqrt{3}+2\sqrt{3}^{n-1}K|d|^n)$ in which here $\varepsilon=|d|/d$. In parallel the stress on a small layer of material at a (virtual) length X from the extremity of the extrudate assumed undeformed (i.e., as if it kept a constant radius) may be estimated

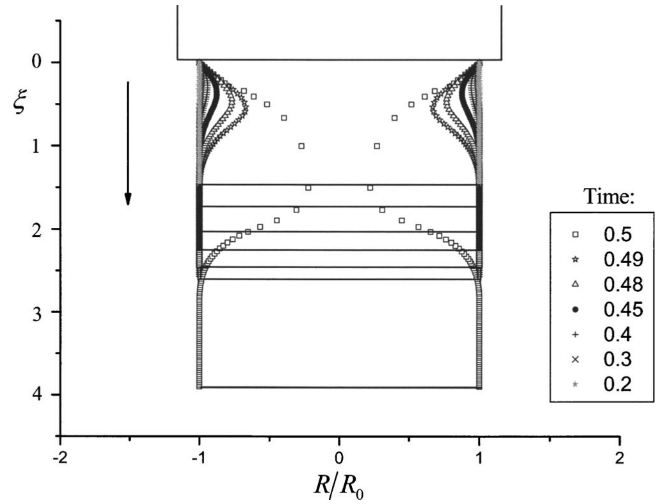

FIG. 4. Dimensionless evolution of the vertical cross section of the extrudate at different times after exit start as predicted by our theory for a simple yield stress fluid (Herschel-Bulkley model with $n=1/3$). Representation in terms of the dimensionless distance from exit $\xi=-x/X_c$ and dimensionless radius R/R_0 as a function of the dimensionless time $(\sqrt{3}\tau_c/K)^{1/n}t/2\sqrt{3}$. The dimensionless exit velocity $[(2\sqrt{3}V/X_c)(K/\sqrt{3}\tau_c)^{1/n}]$ was 2.5.

from the momentum equation: in the vertical direction it results from the weight of the material below, which is equal to $\rho g \pi X R_0^{\,2}\mathbf{e}_z$. Under the elongational flow assumption the stress in the other direction (tangential and radial) are negligible. The local stress tensor thus is expressed as $\mathbf{\Sigma} = \rho g X R_0^{\,2}/R^2 \mathbf{e}_{zz} = \rho g X R_0^{\,2}/3R^2[\mathbf{I}+(-\mathbf{e}_{rr}-\mathbf{e}_{\theta\theta}+2\mathbf{e}_{zz})]$. The second term in the bracket of the right-hand side is the extra-stress tensor. Thus we have $\sqrt{-T_{II}}=\rho g X R_0^{\,2}/\sqrt{3}R^2$ and we deduce from the yielding criterion that the extrudate remains undeformed ($R=R_0$) for a length X smaller than the critical length $X_c=\sqrt{3}\tau_c/\rho g$. For larger values of X the balance between the resulting longitudinal component of the stress tensor and its expression from the constitutive equation gives the relation between time and space variations of the extrudate radius and its extruded length (X):

$$\dot{R} = -\frac{R}{2\sqrt{3}}\left[\frac{\rho g X R_0^{\,2}}{KR^2} - \frac{\sqrt{3}\tau_c}{K}\right]^{1/n}. \tag{1}$$

From the mass conservation the final thickness (dx) of each layer situated at the virtual distance X is related to its initial thickness (dX) via the mass conservation, $R^2 dx = R_0^{\,2} dX$, from which we deduce the effective distance from the extrudate bottom: $x=\int_0^X (R_0/R)^2 dX$. A typical example of the evolution of the extrudate shape in time is shown in Fig. 4. It is worth noting that the minimum radius (R_m) ultimately tends to zero in a very short time, so that the extrudate appears to abruptly separate just after R_m has reached a critical value of the order of $R_0/2$.

These equations predict that the extrudate deforms at each distance $X > X_c$ at a rate increasing with X. However, a layer starts to be deformed later for an increasing X. Thus the effective length of separation increases with the exit velocity V since the extruded length after a given time increases with

V while the rate of strain of a given layer remains constant. More quantitatively, for a given value of X Eq. (1) may be integrated between the initial time of appearance of this material layer (for which the radius is still R_0), namely X/V, and the time $t_c=f(X)$ at which the layer radius would reach zero if this layer was the only one submitted to the weight of material below. The minimum of f is obtained for the dimensionless distance $\lambda=X_0/X_c$ at which the extrudate effectively separates into two parts. It is the solution of

$$\lambda(\lambda-1)^{1/n}=\nu \tag{2}$$

in which $\nu=(K/\tau_c)^{1/n}\rho gV/\tau_c$ is the dimensionless velocity. Two approximate solutions may be explicitly expressed: in the limit of very low exit velocities ($\nu \ll 1$) we have $\lambda \approx 1+\nu^n$; in the limit of large velocities ($\nu \gg 1$) we have $\lambda \approx \nu^{n/n+1}$.

IV. COMPARISON BETWEEN THEORY AND EXPERIMENTS

It appears that Eq. (1) rather well represents the shape of data evolution with flow rate for the gel (see Fig. 2). Moreover, for all materials the extrudate appears to abruptly separate (cf. Fig. 1) just after R_m has reached a critical value of the order of $R_0/2$ in very good qualitative agreement with theoretical predictions. This suggests that our theoretical approach within the frame of a simple yielding behavior for the gel is appropriate and reasonable for the other materials. However, for all materials except the gel there is a strong discrepancy between the theoretical predictions and the experimental data (see Fig. 2): λ is much larger than 1 even at low flow rates and remains more or less constant and tends to increase at large flow rates (ketchup and mayonnaise). This means that the effective behavior of these materials is not that expected from the (rheological) flow curve obtained for a decreasing stress ramp. Let us instead consider the behavior as it appears from the increasing flow curve (see Fig. 3): as a first approximation it may be represented by a pure plastic behavior at a critical shear stress (τ_{c_2}) up to a critical shear rate beyond which it follows a Herschel-Bulkley model with a yielding parameter equal to τ_{c_1}. (Other behavior types, such as a simple power-law model, could also be assumed beyond the critical shear rate, but our interpretation and discussion would be similar.) Such a behavior is consistent with the recent observations both from rheometry [9] and Magnetic Resonance Imaging [10] showing that pasty materials cannot flow at a shear rate smaller than a critical value, so that shear banding likely occurs at lower apparent shear rates in conventional rheometry. Finally such a model predicts a constant (dimensionless) length of separation ($\lambda_c=\tau_{c2}/\tau_{c1}$) of the extrudate up to a critical velocity $v_c=\lambda_c(\lambda_c-1)^{1/n}$ beyond which it starts to increase, in relatively good agreement with our data (see Fig. 2).

In order to represent the behavior observed with the bentonite it would be necessary to further take into account its thixotropic behavior which is more marked than for the other materials: the apparent yield stress for start flow significantly increases with the time of rest before shear (see caption of Fig. 3). For the sake of simplicity let us consider the case of a thixotropic material for which, under slow flow flows, the yield stress increases with time as $\tau_c=\alpha t^p (p<1)$. Then X_c increases in the same way and the extrudate can separate only when the length which came out of the conduit ($X=Vt$) becomes larger than X_c. Neglecting the time of separation, under sufficiently low velocities, the length of separation thus writes $X_0=(\alpha\sqrt{3}/\rho g)^{1/1-p}V^{-p/(1-p)}$, which decreases with the velocity (in the limit of low velocities), in qualitative agreement with our data.

Let us turn back to the string of sausage pattern observed for flow rates larger than Q_c. Basically the same instability as above described in the general case of viscoplastic fluids has time to develop and yields the formation of several successive droplets for large flow rates. However, since the theory predicts an almost instantaneous separation we would not expect this pattern. If it occurs this is because, due to a larger weight of material below it, the drop velocity of the above "sausage" tends to be larger than the beneath "sausage" (situated just below the second one). Thus successive droplets of increasing drop velocities do not have time to separate. A similar effect occurs for simple viscous liquids: at low flow rates surface tension effects induce the separation of the jet in droplets, at slightly larger flow rates this instability takes the form of a string of sausage pattern.

V. CONCLUSION

We have shown that generally the length of separation of a paste falling under its own weight remains constant and starts to increase at large flow rates. This instability is intrinsically related to the peculiar behavior of pastes, which as a first approximation must be considered as pure plastic materials in some range of shear rates including zero. Our study also shows that it is possible to control the characteristics of the extrudate by varying the flow rate, the yield stress, or the thixotropic character of the material. Among others a practical consequence is that it is useless to increase the flow rate in order to avoid ketchup drip. This effect can only be avoided by continuously displacing the jet and keeping the orifice at a distance from the solid surface approximately equal to the separation length so that the sample always partly lies on the plate.

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