

Solid-solid transition in Landau-Levich flow with soft-jammed systems

M. Maillard^a, J. Boujlel^{a,b}, P. Coussot^a

^a*Université Paris-Est, Laboratoire Navier (ENPC-IFSTTAR-CNRS), Champs sur Marne, France*

^b*SVI (Saint-Gobain – CNRS), Aubervilliers, France*

Abstract: We study the Landau-Levich problem, i.e. withdrawal of a plate from a bath of fluid, in the case of a soft-jammed system, which involves a transition from a solid bath to a solid layer stuck on the plate. We show that this solid-solid transition is prepared inside the bath before the emersion from the fluid, through the existence of a uniform (boundary) layer in the liquid regime along the plate. This layer controls the original characteristics of the (solid) coated layer, whose thickness is almost independent of the velocity but proportional to the material yield stress.

PACS: 83.60.La, 47.85.mb, 68.15.+e

Various materials, such as foams, emulsions and colloids are soft-jammed systems, i.e. solid at rest but liquid when submitted to a sufficiently large stress [1]. Under simple flow conditions these properties lead to an original coexistence of solid and liquid phases in the same system [2]. A more complex situation is encountered with such fluids in our everyday life: we commonly extract objects from baths of mud, chocolate, paint, cement paste, cream. In that case we have an original transition from a bath of material at rest, i.e. in its solid state, to a film stuck on the object and thus again in a solid state but with a completely different shape. The characteristics and origin of this “solid-solid” transition are unknown as yet. A wide range of practical operations also involve flows of such fluids initially at rest and partly removed before reaching a new solid state: mixing, injection, formwork filling, coating on walls or skins, etc.

In the case of simple liquids the extraction leads to the well-known Landau-Levich problem. Most studies in that field focused on the film formation and thickness [3-5]. Different flow regimes may be observed inside the bath, but the liquid flows at any point [6], so that the transition from the bath to the surface is smooth.

Here we show that for soft-jammed systems the solid-solid transition is prepared inside the bath, through the existence of a thin (boundary) layer in the liquid regime along the object. This liquid layer also controls the characteristics of the (solid) coated layer, whose thickness is almost independent of the object velocity. This suggests that any complex flow of a jammed system between two solid states is controlled by such a liquid layer.

As (model) soft-jammed systems we used solutions of *Carbopol 980* in water at different concentrations (see [7]). Rheometrical tests carried out with a Bohlin C-VOR rheometer equipped with rough parallel plates show that these materials behave as simple yield stress fluids (without thixotropy). Their flow curve, i.e. steady state shear stress (τ) vs shear rate ($\dot{\gamma}$) data, can be well fitted over the shear rate range $[10^{-2}; 10^2 \text{s}^{-1}]$ by a HB (Herschel-Bulkley) model, namely: $\tau < \tau_c \Rightarrow \dot{\gamma} = 0$ (solid regime); $\tau > \tau_c \Rightarrow \tau = \tau_c + k\dot{\gamma}^n$ (liquid regime);

where k and n are material parameters, and τ_c is the yield stress. However it is critical to keep in mind that transient, reversible deformations can occur in the solid regime. Since at the different concentrations we found a constant value for n (≈ 0.35) and values for τ_c/k in a limited range (between 1.9 and 2.8), in the following we describe the materials only through their yield stress value. We carried out experiments with 10 materials with $\tau_c \in [9-82 \text{ Pa}]$.

We study the vertical displacement at a constant velocity V in the range $[0.1-17 \text{ mm.s}^{-1}]$, of a 25 cm long plate initially immersed in a fluid bath at rest in a container. The vertical plate is linked to a dual-column testing system (*Instron 3365*) which controls the position with a resolution of 0.1 μm . The apparatus is equipped with a 10 N static sensor able to measure the force within a relative value $\pm 10^{-6}$ of the maximum value. In order to avoid wall slip effects we covered the surface of the plate with waterproof sandpaper with an effective roughness of a few tenths of microns, a thickness much larger than the elements suspended in the liquid. The width of the plate was always much larger than the coated layer which supports the assumption of a 2D flow.

We start by studying the macroscopic flow characteristics, i.e. the coated layer. In such a situation, for simple liquids (of viscosity μ) at constant velocity a uniform film forms along the plate, the thickness (h) of which mainly varies as a power-law of the capillary number ($Ca = \mu V / \sigma$, in which σ is the fluid surface tension) as long as gravity effects are negligible [3-5]. A very limited number of (phenomenological) studies concerned non-linear fluids. It was shown that elastic effects tend to increase h [8-9]. For a shear-thinning behavior a thickness increase [10] or decrease [11] was observed when the power-law index decreases. For yield stress fluids some numerical simulations [12-13] suggested that h increases with τ_c . A theoretical analysis [14] in the case of dominant yielding effect (i.e. plastic flow) and negligible gravity effects finally predicted $h \propto \tau_c^2$.

Here a test consists in driving the plate through the bath down to some depth then moving it back upwards. We

checked that a time at rest before motion inversion had no impact on the results. After the exit from the bath at a given velocity the fluid deposit appears to be uniform beyond a few centimeters from the edges (see left inset of Fig. 1). Moreover, after plate exit, this layer remains stuck on the plate and rigid, i.e. no drainage occurs. Thus the uniformity of the layer can be proved from measurements of its weight after extraction following immersion at different depths: the weight difference is proportional to the immersion depth difference. We used this technique to determine, with an uncertainty of 15%, the thickness h of the uniform region. h appeared to be independent of the plate thickness when the latter was varied in the range [1-10 mm].

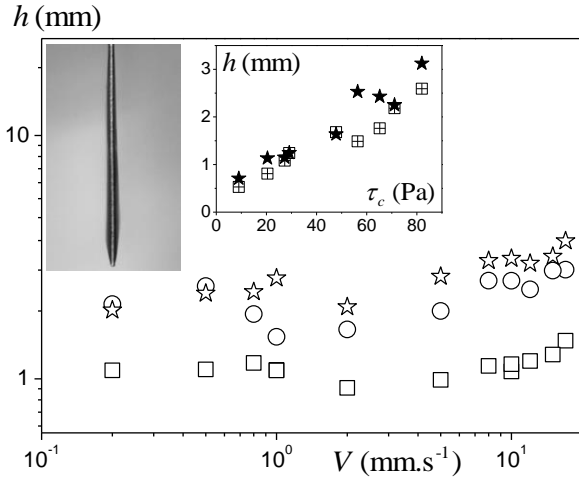


Figure 1: Thickness of the coated layer after dip coating process as a function of V for different yield stress fluids: (squares) 27 Pa, (circles) 56, (stars) 82 Pa. The left inset shows a side view of the coated layer on the plate (height: 12 cm). The right inset shows the coated thickness as a function of the yield stress for $V = 1$ mm/s (cross-squares) and for $V = 10$ mm/s (stars).

A first striking result is that h is only slightly dependent of V in our range of tests: h increases by a factor of less than 2 when V increases over two decades. This strongly contrasts with the observed variations as a power law of V with an exponent $2/3$ in the viscous-capillary regime and an exponent $1/2$ in the viscous-gravity regime for Newtonian fluids [3-4]. Moreover there seems to be a horizontal asymptote at low velocities: h tends to a finite value at vanishing velocity (see Fig. 1). Thus, due to the absence of drainage the dip-coating process for usual yield stress fluids cannot provide a coated layer thickness smaller than a critical value h_c . Finally h mainly varies with τ_c ; for a given V we roughly have $h \propto \tau_c$ (see right inset of Fig. 1).

Actually the stoppage of a layer of such a finite thickness is a usual characteristic of free surface flows of yield stress fluids. For the steady uniform flow along a vertical surface the momentum equation provides the shear stress distribution, i.e. $\tau = \rho g(h - y)$, in which y is the distance from the plate, ρ the fluid density and g the gravity. Thus the maximum shear stress, situated along the plate, is ρgh , which implies that the fluid

stops flowing if $\tau < \tau_c$, i.e. if $h < h_0 = \tau_c / \rho g$. In our experiments h appears to about three times larger than h_0 . Thus the coated layer is much smaller than expected from a simple vertical gravity flow of a yield stress fluid. This in particular explains why the fluid stops flowing as soon as it is situated along the plate after its exit from the bath: the only external force now acting on it is gravity, which is always smaller than the force associated with τ_c .

Finally two main trends are observed: a significant increase of the coated thickness with the yield stress and a slow increase with the velocity. In this context we can see the apparent plateau level of h at vanishing velocity, i.e. h_c , as a basic characteristics of the process for a given fluid. We directly obtain rough estimations (say, within 20%, due to significant data scattering at low velocities) of h_c from data such as shown in Figure 1. This parameter appears to be well represented (see inset of Fig.2) by

$$h_c \approx 0.3\tau_c / \rho g \quad (1)$$

Moreover the variations of h with V mean that the fraction of material in the liquid regime increases, an effect which should be described in a general way by the Bingham number, which characterizes the relative impact of the two viscous components in the HB model, i.e. τ_c and $k\dot{\gamma}^n$: $Bi = \tau_c h^n / kV^n$. The whole set of data in terms of h/h_c vs Bi indeed align along a single master curve, with an uncertainty of 20% (see Fig.2).

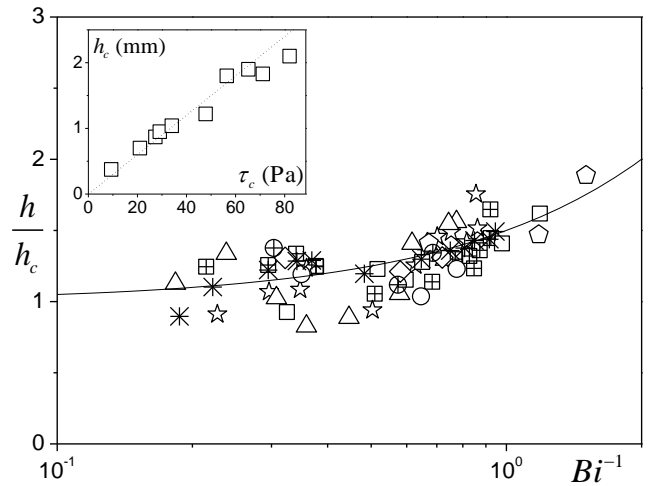


Figure 2: Coated thickness scaled by the critical thickness as a function of Bi^{-1} for the different fluids of yield stress: 9 (pentagons), 21 (squares), 27 (cross-squares), 29 (diamonds), 34 (asterisks), 48 (cross-circles), 56 (triangles), 65 (squares), 71 (circles), and 82 Pa (stars). Continuous line: eq.(2). Inset: critical thickness as a function of yield stress. Dotted line: eq.(1).

Besides the ratio of τ_c to the typical surface tension stress provides the capillary number for such fluids: $Ca_y = \tau_c h / \sigma$. It was recently shown [15] that surface tension effects govern the flow if $Ca_y < 0.1$ and that for

Carbopol gels $\sigma \approx \sigma_{water}$. Here Ca_y is in the range [0.07-4] which means that capillary effects might play some role in the first part of the range and would be fully negligible otherwise. However eq.1 multiplied by h_c leads to $h_c \propto \sqrt{Ca_y}$ over the whole range. This suggests that these are not primarily capillary effects but viscous effects (through τ_c) which are anyway dominant in our tests. This explains that the previous theory [14] which assumes that surface tension effects are important fails to predict our observations.

Since the coated thickness does not directly result from the vertical free surface gravity flow along the plate or from the competition between surface tension and viscous effects around the interface with air, we conclude that the coating process is governed by the flow *before* the emersion from the bath.

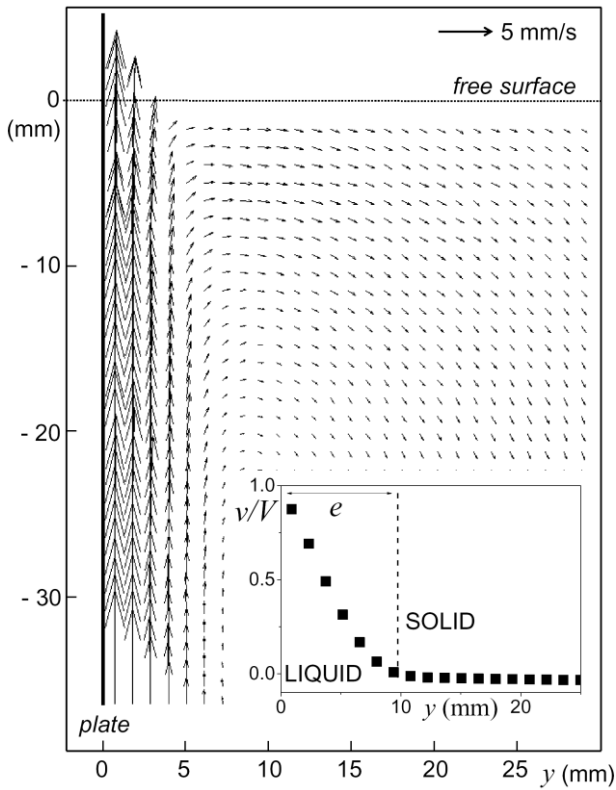


Figure 3: Dip coating of a yield stress fluid ($\tau_c = 34$ Pa): velocity field inside the bath for $V=15$ mm/s. The arrow length is proportional to the velocity modulus, the scale is shown on the right angle of the graph. The inset shows the steady uniform profile of the longitudinal velocity measured beyond 4 cm from the free surface. The vertical dotted line shows the position of the interface between the liquid layer and the solid region.

In order to get an insight in this process we measured the velocity field in the fluid with PIV (Particle Imaging Velocimetry). Polystyrene beads (80 μ m) which served as markers and negligibly affected the rheological behavior of the fluid, were dispersed in the fluid. Their density was very close to that of the fluid so that sedimentation was negligible. Particle motions were observed in a plane perpendicular to the plate and along its central axis enlightened with a laser sheet. For data analysis we used the commercial Software *DaVis*.

A typical velocity field is shown in Figure 3. The fluid is strongly sheared upwards along the plate while it slowly moves downwards at some horizontal distance from the plate, a motion which balances the coated fluid extraction from the bath. A close inspection of data shows that at far from the edges (free surface and plate tip) the longitudinal (vertical) velocity profile is uniform along the plate. Moreover, as for immersion flows of similar yield stress fluids [16], it may be shown from an estimation of the total deformation undergone by the fluid elements along their path, that the fluid is in its liquid state only in a small region (“liquid layer”) close to the plate (see Fig. 3). Beyond that distance the other slight relative motions in the uniform velocity field are small reversible deformations in the solid regime of the material.

The general aspect of the velocity profiles in the liquid layer along the plate is similar to those found for an immersion flow with the same geometry [16]. The sheared thickness (e) increases very slowly with V [17] and seems to tend to a finite value towards vanishing velocities. For small V the slope of the velocity profile is constant, i.e. the shear rate is uniform, over the whole thickness; for the largest V in our range, there is an additional slight curvature close to the liquid-solid interface (see example of Fig.3).

Finally the variations of the liquid layer thickness inside the bath have some similarities with those of the coated layer on the plate (cf. Fig. 1): h is apparently proportional to e (by a factor 1/6.7) (see Fig. 4).

A further look at the velocity field around the free surface shows that the fluid in the liquid layer inside the bath separates into two parts when it approaches the free surface (see Fig. 3): some fluid volume still moves along the plate and will ultimately move as a whole with the plate after its exit from the bath; the rest of the liquid layer turns and moves away from the plate along the free surface. The coated layer is thus some fraction of the liquid layer inside the bath. Moreover the two fluid parts eventually fall back in a solid regime, either in the bath or along the plate.

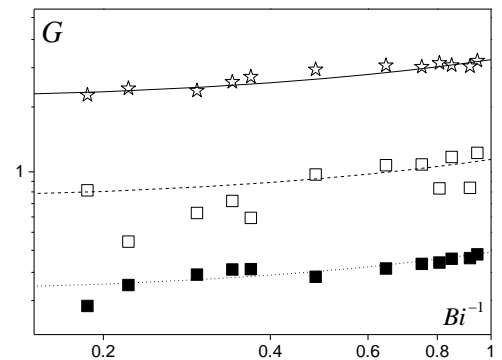


Figure 4: Dip coating of a yield stress fluid ($\tau_c = 34$ Pa): thickness of the coated layer (h) (filled squares), the liquid layer (e) (stars), and the equivalent flow rate thickness (z) in the liquid layer (open squares) scaled by $\tau_c / \rho g$ (G) as a function of Bi^{-1} . Continuous line: model of the text for e ;

dotted line: equation (2). The dashed line corresponds to this line times a factor 2.5.

In order to compare the flow characteristics of the liquid and the coated layers we describe the flow rate of the liquid layer through its equivalent thickness z if all the fluid was moving at V , in other words z is the liquid layer flow discharge per unit width and scaled by V . From the measured velocity profiles z appears to be proportional to h by a factor around 2.5 (see Fig. 4). That means that the liquid layer separates into two parts: about 40% stuck along the plate and 60% remaining in the bath.

Since the coated layer has a thickness proportional to the liquid layer thickness and represents about 40% of the total flow rate in this liquid layer, the prediction of h requires some knowledge of the characteristics of this liquid layer. In that aim we can develop a simple model based on our general knowledge of the qualitative flow characteristics. Let us look at the problem in the frame of reference attached to the plate. We assume that all the material around the liquid layer in the container is in its solid regime. Since it is lying on the container this material volume moves downwards as a rigid block with the container. Thus, in contrast with a free surface flow over an inclined plane for which the (solid) plug (in contact with the free surface) is entirely supported by the liquid region and drags it, here the solid region is entirely supported by the container. Under these conditions we can consider that the material in the liquid layer flows essentially as a result of gravity inside a layer of thickness e and with a velocity difference V between the two sides of the layer. In this situation the viscous (energy) dissipation per unit length and width of plate is balanced by the gravity work per unit time:

$$\int_0^e \tau \dot{\gamma} dy = \int_0^e \rho g v dy, \text{ in which } v \text{ is the local velocity.}$$

Inside the liquid layer the shear rate is by definition different from zero everywhere, which also contrasts with a uniform free surface flow which always contains a plug along the free surface. As a first approximation we assume that the shear rate $\dot{\gamma}$ is uniform in the liquid layer, i.e. it is equal to V/e . The energy balance then writes $\tau \dot{\gamma} e = \rho g e V / 2$, with τ given by the HB equation, which leads to $G_e = 2(1 + Bi_e^{-1})$, with $G_e = \rho g e / \tau_c$ and $Bi_e = \tau_c e^n / k V^n$. This result is in excellent agreement with our measurements (see Fig.4), which confirms the validity of this simple model.

Moreover, if we use the above mentioned empirical observation, i.e. $h = \alpha e$ in which α is a thinning factor here equal to $1/6.7$, we deduce a general expression for the coated thickness:

$$h/h_0 \approx 2\alpha(1 + (\alpha^n Bi^{-1})) \quad (2)$$

which is consistent with our measures of h_c leading to eq.(1), and well represents our master curve for all data (see Fig.2).

Let us now consider that the coated layer motion is associated with a fraction x of the flow rate (Q) of the liquid layer per unit plate width. The above fraction corresponds to the material situated between 0 and a distance A such that $\int_0^A v dy = xQ$. For a homogeneous shear rate we have $Q = \int_0^e v dy = eV/2$. Finally the thickness of this layer when it moves as a plug at the velocity V writes $1/V \int_0^A v dy = xe/2$ and we deduce $h = (x/2)e$. The value for α obtained from the value estimated for x (40%) from our measurements, i.e. $1/5$, is larger than the effective value, i.e. $1/6.7$. The latter value would require $x = 30\%$. This discrepancy might be due to uncertainties on the velocity profile measurements and to the fact that the real velocity profiles are not strictly linear.

We now have a clear view of the process allowing the solid-solid transition: the development of a liquid layer allows this transition and controls the thickness of the coated layer, so that the coating process is governed by the flow before the emersion from the bath. Our simple model which well predicts the experimental observations relies on only one empirical data, namely how the fluid separates at the free surface, which is at the origin of the thinning factor α . Sophisticated numerical simulations might provide further information on the origin of this value.

More generally our results show that complex flows of yield stress fluids must be considered in the frame of new fluid mechanics concepts possibly relying on the identification of the boundary layer characteristics.

References

- [1] A.J. Liu, S.R. Nagel, *Nature*, 396, 6706 (1998)
- [2] P. Coussot et al., *Phys. Rev. Lett.*, 88, 218301 (2002); D. Bonn and M.M. Denn, *Science*, 324, 1401 (1999); T. Divoux, D. Tamarii, C. Barentin, S. Manneville, *Phys. Rev. Lett.*, 104, 208301 (2010)
- [3] K.J. Ruschak, *Ann. Rev. Fluid Mech.*, 17, 65 (1985)
- [4] D. Quéré, *Ann. Rev. Fluid Mech.*, 31, 347 (1999)
- [5] J. H. Snoeijer, J. Ziegler, B. Andreotti, M. Fermigier, and J. Eggers, *Phys. Rev. Lett.*, 100, 244502 (2008)
- [6] H. C. Mayer, R. Krechetnikov, *Phys. Fluids*, 24, 052103 (2012)
- [7] P. Coussot et al., *J. Non-Newton. Fluid Mech.*, 158, 85 (2009)
- [8] A. de Ryck, and D. Quéré, *Langmuir*, 14, 1911 (1998)
- [9] J. Ashmore, A.Q. Shen, H.P. Kavehpour, H.A. Stone, G.H. McKinley, *J. Eng. Math.*, 60, 17 (2008)
- [10] F. Kamisli, *Chem. Eng. Processing*, 42, 569 (2003)
- [11] C. Gutfinger, and J.A. Tallmadge, *AIChE*, 11, 403 (1965)
- [12] P. Hurez, and P.A. Tanguy, *Polymer Eng. Sci.*, 30, 1125 (1990)
- [13] A. Filali, L. Khezzar, E. Mitsoulis, *Computers & Fluids*, 82, 110 (2013)
- [14] B.V. Derjaguin and S.M. Levi, *Film coating theory* (The Focal Press, London, 1964)
- [15] J. Boujlel, and P. Coussot, *Soft Matter*, 9, 5898 (2013)
- [16] J. Boujlel, M. Maillard, A. Lindner, G. Ovarlez, X. Chateau, P. Coussot, *J. Rheol.*, 56, 1083 (2012)
- [17] T. Chevalier, S. Rodts, X. Chateau, J. Boujlel, M. Maillard, P. Coussot, *EPL*, 102, 48002 (2013)