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SHORT COMMUNICATION

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Spreading of viscous droplets on a non viscous liquid

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Abstract Some polymer melts (of high viscosity η) can wet completely the surface of a non miscible, simple liquid. We discuss here the laws of spreading for a macroscopic droplet of this type, when the internal friction of the droplet dominates. We predict a droplet radius increasing like $t^{1/4}$ where t is the spreading time, or equivalently a droplet curvature decreasing like t^{-1}. The droplet should be surrounded by a precursor film, which is not discussed in the present note.

Key words Wetting – liquid interfaces – polymer melts – droplets – plug flows

Introduction

The spreading of macroscopic droplets on completely wettable solids was studied experimentally long ago by Tanner [1]. In his case the spreading radius $R(t)$ increased very slowly, like $t^{1/10}$. One can also measure the focal length of the lens formed by the droplet, or equivalently the curvature C of its free surface, and one finds $C \approx t^{-2/5}$ which follows from the proportionality between C and h/R^2 (where h is the droplet thickness), and from the condition of constant volume. These laws have been interpreted theoretically [2]: most of the interfacial energy S which is recovered upon wetting is burned inside a precursor film, and the remaining driving force, pulling the droplet outwards, is simply $\gamma(1 - \cos\theta) \cong \gamma\theta^2/2$ where γ is the surface tension and θ is the dynamic contact angle. This driving force is balanced by viscous stresses which are relatively strong because of the large velocity gradient between top and bottom of the droplet.

We want to discuss here a different situation, where the droplet is lying on top of a liquid substrate of low viscosity η_s. We than have a plug flow inside the spreading droplet (Fig. 1) and we expect Tanner's law to be deeply modified. In Section II we show this at the level of scaling laws. But it turns out that the hydrodynamic problem is soluble exactly (in the long time limit, where a lubrication approximation can be used): this is explained in Section III. Various physical implications are discussed in Section IV.

The spreading droplet shown on the figure is assumed to be very thin and shown on the figure. One (minor) difference with the case of a solid substrate is that the interface between the polymer melt P and the supporting liquid is not strictly flat, but is curved, with a profile $z_2(r)$. For the moment we consider small droplets, for which gravity effects are negligible. Then the Laplace condition applied on the top side (profile $z_1(r)$) and on the bottom side (profile $z_2(r)$) gives:

$$\gamma_1 \nabla^2 z_1 = \gamma_2 \nabla^2 z_2 \tag{1}$$

where γ_1 is the air/P interfacial tension, and γ_2 is the L/P interfacial tension. This condition can be integrated to give $\gamma_1 \nabla z_1 = \gamma_2 \nabla z_2$ (with no integration constant since both slopes vanish at the center of the droplet). Using this one can show that the capillary energy takes the form:

$$\tfrac{1}{2}[\gamma_1(\nabla z_1)^2 + \gamma_2(\nabla z_2)^2] = \tfrac{1}{2}\gamma(\nabla z)^2 \tag{2}$$

$$\gamma^{-1} = \gamma_1^{-1} + \gamma_2^{-1} \tag{3}$$

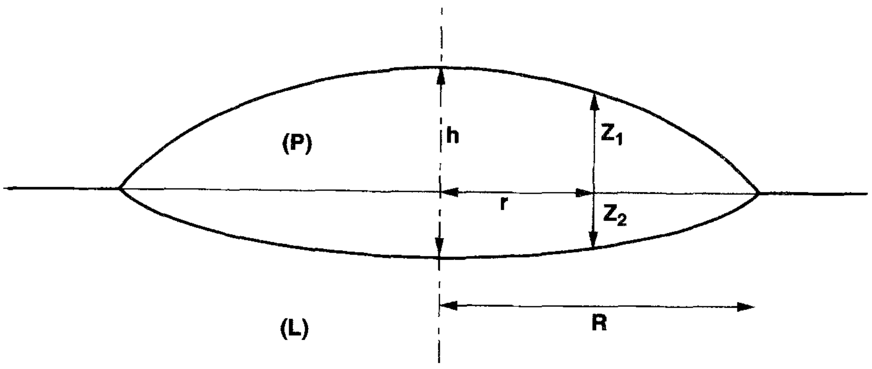

Fig. 1 Profile of a polymer drop (*P*) spreading on an immiscible liquid (*L*) of low viscosity. This figure applies when the weight of (*P*) is negligible. For larger weights the profile becomes flat in the center region ("pancake" regime)

with $z = z_1 + z_2$, and the tensile force at the edge is:

$$\gamma_1 \frac{\theta_1^2}{2} + \gamma_2 \frac{\theta_2^2}{2} = \frac{1}{2}\gamma\theta^2 . \tag{4}$$

Thus we can think in terms of a single variable $z(r, t)$, and a single edge angle θ, provided that we renormalise the interfacial tensions.

Scaling laws

The velocity gradients are of order $\dot{R}/R$ (where $\dot{R} = dR/dt$) and the viscous dissipation in the droplet is (ignoring all coefficients):

$$T\dot{S} \approx \Omega\eta\left(\frac{\dot{R}}{R}\right)^2 , \tag{5}$$

where $\Omega \cong hR^2$ is the droplet volume, and is constant (no evaporation). Equating this to the work of the driving force:

$$2\pi R\dot{R}\gamma\frac{\theta^2}{2} = T\dot{S} , \tag{6}$$

we arrive at

$$R^4 \cong V^* t\Omega , \tag{7}$$

where $V^* = \gamma/\eta$ is a characteristic velocity. The curvature C of the upper surface is of order $C \approx h/R^2$ (where h is the droplet thickness)

$$C \approx \frac{\Omega}{R^4} \approx \frac{1}{V^* t} . \tag{8}$$

This law could be checked accurately by measurements of the focal length of the lens formed by the droplet.

This scaling approach also allows us to see how viscous the polymer must be for the dissipation (5) to be dominant: assume that the supporting liquid L has a thickness $e > R$ and a small viscosity η_s. Then the dissipation in L is due to shear rates over volumes $\approx R^3$:

$$T\dot{S} \cong R^3\eta_s\left(\frac{\dot{R}}{R}\right)^2 . \tag{9}$$

Comparing Eqs. (9) and (5), we see that our regime should hold provided that $\eta > \eta_s(R/h)$. If we reverse this inequality we return to another regime already discussed by Joanny [3].

Detailed profiles

In the lubrication approximation, the velocity field $\vec{v} = (v_x, v_y)$ inside the droplet is two dimensional, and satisfies the conservation equation:

$$\frac{\partial z}{\partial t} + div(z\vec{v}) = 0 \tag{10}$$

where z is the local thickness. The velocity is ruled by a two dimensional Navier–Stokes equation (in the viscous limit)

$$0 = \eta\nabla^2\vec{v} - \nabla p , \tag{11}$$

where the pressure p is of the Laplace form:

$$p = p_a - \gamma\nabla^2 z , \tag{12}$$

where p_a is the atmospheric pressure.

For our problems (with a radial velocity $\vec{v}$) $\operatorname{curl}\vec{v} = 0$ and $\nabla^2\vec{v} = \nabla div\,\vec{v}$. Thus, Eq. (11) may be integrated in the form:

$$\eta\, div\,\vec{v} + \gamma\nabla^2 z = p_1 , \tag{13}$$

where p_1 is a constant, which we might call the squeezing pressure. It is the leading term for the problem of squeezing a fluid between two plates. But for our problems, the only source of energy is γ and $p_1 = 0$. One can then integrate once more Eq. (13) and reach:

$$\vec{v} = -V^*\nabla z . \tag{14}$$

(There is no integration constant because both $\vec{v}$ and ∇z vanish at the center of the droplet.) Returning to Eq. (10) we arrive at a non linear diffusion equation:

$$\frac{\partial z}{\partial t} = \nabla[D(z)\nabla z] , \tag{15}$$

where $D(z) = V^* z$ is a local diffusion coefficient. The solution turns out to be simple:

$$z(r,t) = \frac{2}{\pi}\frac{\Omega}{R^2}\left(1 - \frac{r^2}{R^2}\right) \tag{16}$$

with a condition on R which is a precise version of Eq. (7)

$$R^4 = \frac{16}{\pi}\Omega V^* t . \tag{7'}$$

Concluding remarks

1) All our discussion was restricted to small drops, where gravity effects are negligible: sizes $< \kappa^{-1} = (\gamma/\rho g)^{1/2}$ where ρ is the density and g the gravitational acceleration. In the opposite limit of very large drops, the shape is essentially described by a flat pancake, of constant thickness h. The gravitational energy is:

$$F_g = \tfrac{1}{2}\tilde{\rho} g h^2 \pi R^2 , \tag{17}$$

where $\tilde{\rho}$ is the density corrected for the Archimede's pressure: $\tilde{\rho} = \rho_p(1 - \rho_p/\rho_L)$. Equation $\dot{F}_g$ with the dissipation of Eq. (5), we arrive at the scaling law:

$$R\dot{R} \cong \tilde{\rho} g \Omega/\eta \tag{18}$$

giving $R \approx t^{1/2}$. This must be supplemented by a description of the edge of the pancake, which is expected to show a dynamic contact angle $\theta \approx \dot{R}/V^*$ (the local analog of Eq. (14)).

2) An interesting variant of our problem is obtained with a polymer on a solid surface, in the special regime where the surface is nearly ideal: following the arguments of ref. [4], we then expect a strong slippage of the melt on the surface, characterized by a large "extrapolation length" b. If $b \gg R/\theta$ Eq. (7) should hold, because the dissipation inside the droplet overcomes the solid/liquid friction.

3) As usual in condition of complete wetting, we expect a precursor film, with a thickness in the range of 10 nanometers. This film should expand with velocities much larger than $\dot{R}$. We postpone the discussion of this precursor to a later publication.

References

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