*J. Fluid Mech.* (2004), *vol.* 513, *pp.* 77–85. © 2004 Cambridge University Press
DOI: 10.1017/S0022112004000278 Printed in the United Kingdom

# Spreading of non-Newtonian fluids on hydrophilic surfaces

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(Received 5 April 2004 and in revised form 2 June 2004)

The spreading of Newtonian fluids on smooth solid substrates is well understood; the speed of the contact line is given by a competition between capillary driving forces and viscous dissipation, yielding Tanner's law $R \propto t^{1/10}$. Here we study the spreading of non-Newtonian liquids, focusing on the two most common non-Newtonian flow properties, a shear-rate dependence of the viscosity and the existence of normal stresses. For the former, the spreading behaviour is found not to deviate strongly from Tanner's law. This is quite surprising given that, within the lubrication approximation, it can be shown that the contact line singularity disappears due to the shear-dependent viscosity. The experiments are compared with the predictions of the lubrication theory of power-law fluids. If normal stresses are present, again only small deviations from Tanner's law are found in the experiment. This can be understood by comparing viscous and normal stress contributions to the spreading; it turns out that only logarithmic corrections to Tanner's law survive, which are nonetheless visible in the experiment.

## 1. Introduction

The spreading of a droplet on a smooth solid surface has received much attention because of the singularity that occurs at the contact line (Huh & Scriven 1971) and its importance for a large number of applications. The radius $R$ of the drop grows according to Tanner's law (Tanner 1979): $R(t) \propto t^{1/10}$. Tanners's law reflects the competition between capillary forces whose amplitude is given by the surface tension $\sigma$ and viscous dissipation given by the viscosity $\eta$. The final result for the spreading rate also involves the volume of the drop $\Omega$ and is $R(t) = \Omega^{3/10}(\sigma/\eta)^{1/10}t^{1/10}$. This classical result is well-established. However, the value of the prefactor is still controversial and differs according to the model used for contact line motion (for reviews see Dussan V. 1979; de Gennes 1985; Pomeau 2002; for a discussion of this matter see Eggers & Stone 2004).

The spreading of non-Newtonian liquids is much less well understood. The main challenge in the problem of the spreading of non-Newtonian fluids is that the constitutive equation is nonlinear (Rosenblat & Davis 1985). Most theoretical studies have used simple constitutive equations, focusing on shear-thinning behaviour (Gorodtsov 1989; King 2001*a,b*; Starov *et al.* 2003; Neogi & Ybarra 2001; Betelú & Fontelos 2003). Shear thinning was even proposed as suppressing the singularity at the contact line (Weidner & Schwartz 1994; Ansini & Giacomelli 2002; Carré & Woehl 2002). The first attempts to account for other non-Newtonian properties concluded that normal stress effects were unimportant (Neogi & Ybarra 2001; Rosenblat & Davis 1985). From the experimental side, we know of only a single experimental study in which the spreading of a polymer solution at only one concentration was studied (Carré & Eustache 1997, 2000). Small deviations from Tanner's law were reported, and associated with the shear-thinning behaviour of the solution.

Most non-Newtonian fluids encountered in practice exhibit a number of different non-Newtonian properties, making it difficult to attribute deviations from the Newtonian result to a specific non-Newtonian flow property. Notably, concentrated polymer solutions (such as the one used in the experiments of Carré & Eustache 1997) often exhibit both shear-thinning and normal stress effects. Here we attempt to disentangle the influence that different non-Newtonian flow properties have on the spreading. To do so, we study spreading in two different dilute or semi-dilute polymer solutions, that each exhibit only one non-Newtonian property, in the sense that other non-Newtonian effects can be neglected. For solutions of flexible polymers, elastic effects such as normal stresses and a large elongational viscosity are dominant, whereas the shear viscosity is almost constant. Stiff polymers, on the other hand, may show a strong shear rate dependence of the viscosity, but almost negligible elastic effects (i.e. normal stresses). We study the spreading of these two model solutions as a function of polymer concentration, in order to change the size of the non-Newtonian effects. In addition, we characterize the non-Newtonian flow properties of these polymer solutions completely, allowing separate and quantitative investigation of the influence of the two most common non-Newtonian properties on the spreading: shear thinning and normal stress effects. We compare the experimental results with the lubrication theory for power-law fluids, and with a simple law accounting for normal stresses.

## 2. Experiment

### 2.1. *Parameters*

The rheology of the polymer solutions was studied on a Reologica Stress-Tech rheometer equipped with a normal force transducer (cone–plate geometry). We use a large cone (55 mm) with a small angle (0.5°) in order to be able to detect small normal stress differences at high shear rates. The temperature at which experiments were performed was $20 \pm 1^\circ$C. Pure water is provided by a Milli-Q Plus system.

For the experiments on rigid polymers (shear-thinning polymer solution), we use solutions of Xanthane, a stiff rodlike polysaccharide with an average molecular weight of $M_w = 3 \times 10^6$ g mol$^{-1}$, obtained from Aldrich. Rheological measurements show that the overlap concentration $c^*$ is 50 w.p.p.m. (parts per million per weight), so that the measurements presented below are in the dilute and semi-dilute regime. The surface tension for the air/Xanthane solution is $72 \pm 2$ mN m$^{-1}$ at 20°C (Lindner, Bonn & Meunier 2000), independent of polymer concentration over the range of concentrations used in our experiments and thus very close to the surface tension of pure water ($72.7 \pm 2$ mN m$^{-1}$). The rheological characteristics of the xanthane were determined; we observe shear-thinning for shear rates lying between 10 and 1000 s$^{-1}$ and a polymer concentration above 50 p.p.m. We describe the shear-thinning behaviour by a shear rate dependence of the viscosity as $\eta = a\dot{\gamma}^{-\alpha}$, where $\dot{\gamma}$ is the shear rate and the power factor $\alpha$ is positive reflecting the shear-thinning property of the fluid (figure 1*a*). Normal stresses are so small that they are not measurable.

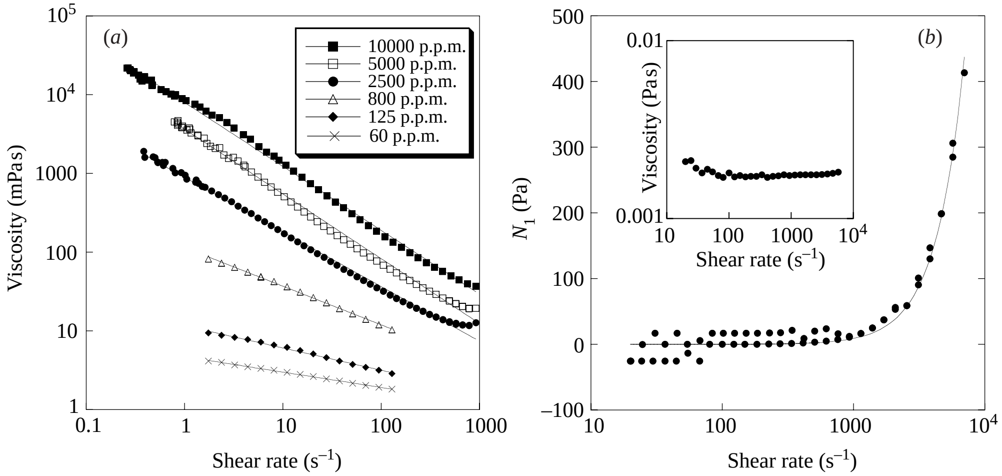

FIGURE 1. (*a*) Viscosity versus shear rate: a power law describes the shear-thinning behaviour of xanthane solutions ($\eta = a\dot{\gamma}^{-\alpha}$). (*b*) PAA solutions exhibit normal stress when subjected to shear whereas viscosity remains almost constant. Quadratic fits give the first normal stress coefficient $\psi_1$ ($N_1 = \psi_1\dot{\gamma}^2$).

For the experiments on flexible polymers, we use polyacrylamide (PAA) from Sigma; its molecular weight is $M_w = 4 \times 10^6$ g mol$^{-1}$. Rheological measurements show that the overlap concentration c* is 400 w.p.p.m., so that the measurements presented below are again in the dilute and semi-dilute regime. The surface tension for the air/PAA solution is found to be $68 \pm 2$ mN m$^{-1}$, and is again found to be independent of polymer concentration over the range of concentrations used in our experiments. The slight lowering of the surface tension with respect to that of pure water indicates that some adsorption (either of the polymer or of some impurities) takes place at the air/solution interface. The PAA solutions have an almost constant shear viscosity, but do exhibit normal stresses. The normal stress $N_1$ is related to the shear rate via the first normal stress coefficient $\psi_1$: $N_1 = \psi_1\dot{\gamma}^2$ (figure 1*b*).

We use mica as a hydrophilic substrate because of its molecular smoothness. We carefully split mica foils in order to obtain clean and smooth surfaces. If the splitting goes wrong, one can observe steps on the mica surface, and their effects on the macroscopic shape of the drop are easily seen: the contact line is pinned on the defects of the surface, and the droplet is no longer circular. We discard all data for which the droplet is not circular.

Using a microsyringe, we form small drops of few microlitres. These are gently deposited on the mica slide. Figure 2 shows a typical picture of the droplet. The droplets are captured by a CCD camera coupled to a computer. This allows measurements of their radius $R$ as a function of time.

### 2.2. *Results*

As a reference experiment, the spreading of a droplet of pure water on mica is found to closely follow Tanner's law over the range of times and radii covered in the experiments. This means that the droplets are small enough for gravity effects to be small, and that spurious effects due to evaporation of the liquid are also unimportant.

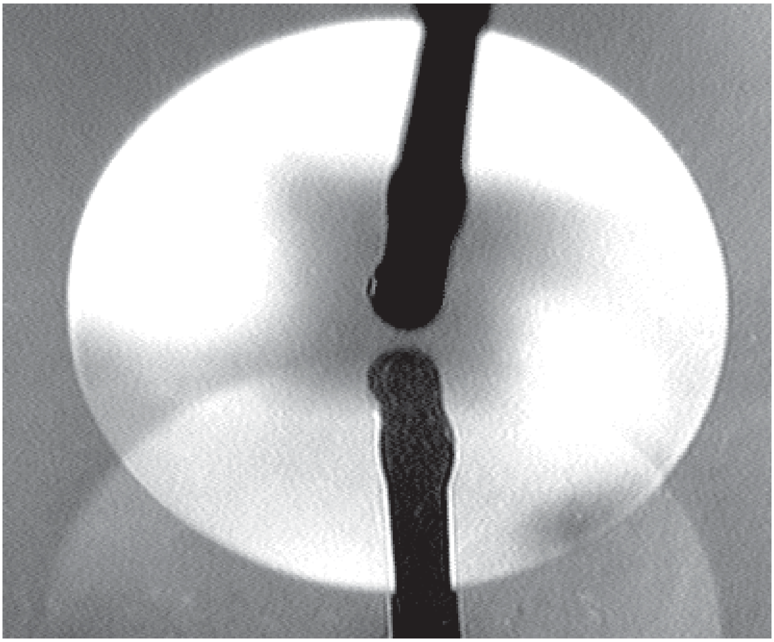

Figure 2. Spreading droplet imaged from above. The size is typically centimetric.

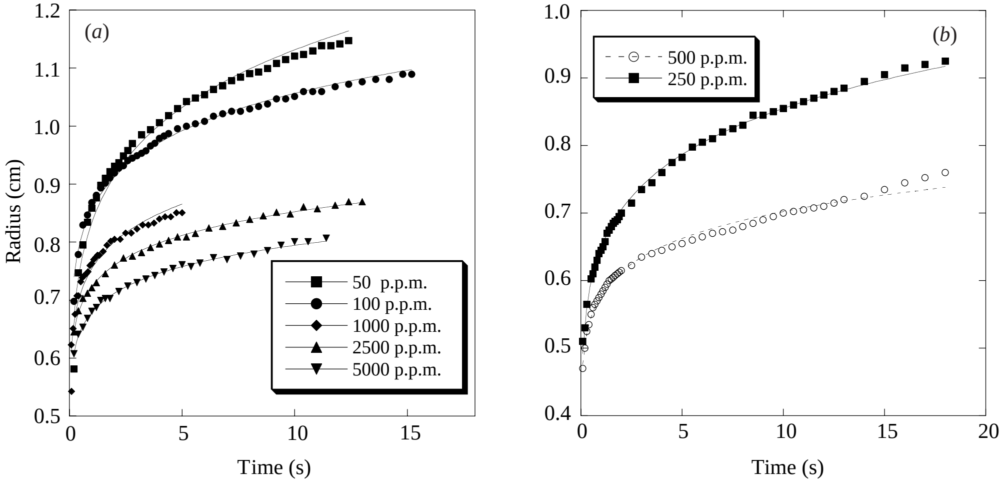

Figure 3. (*a*) Measured radius of xanthane droplets versus time. The solid lines represent power-law fits. (*b*) Measured radius of PAA droplets versus time. The solid lines represent power-law fits; the exponents are slightly smaller than 0.1.

The spreading of the shear-thinning fluid is found to be slightly slower than that of a Newtonian fluid: we observe a power in the spreading law that is smaller than 0.1. We find that the spreading of the non-Newtonian fluid can be characterized by fitting a law of the form:

$$R(t) = Ct^n.$$

The fit (figure 3*a*) then yields the spreading exponent $n$ (figure 4*a*) and the prefactor $C$ (figure 4*b*) for different polymer concentrations. In order to make the link with the

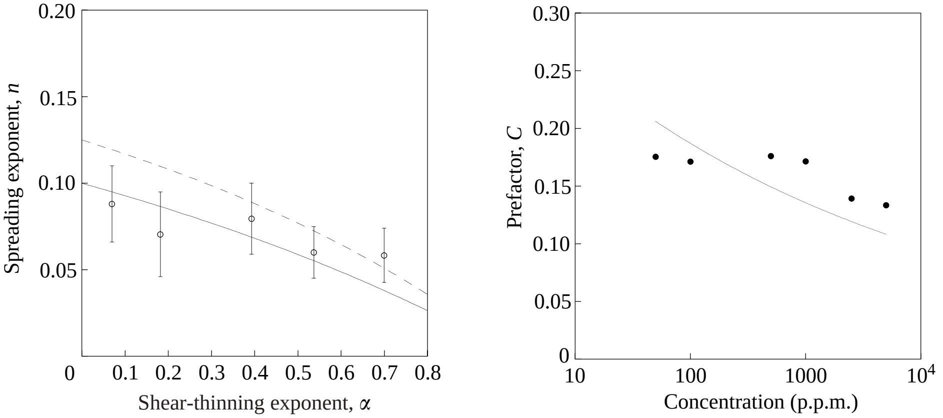

FIGURE 4. Spreading exponent $n$ (*a*) and prefactor $C$ (*b*) for xanthane solutions deduced from figure 3 (*a*) and comparison to theoretical predictions (equation (3.4). The dashed line in (*a*) is the result equivalent to equation (3.4) but with gravitational forces driving the spreading.

rheology we recall that the shear-thinning exponent $\alpha$ is an increasing function of polymer concentration. We therefore observe that the power of the evolution of the radius decreases with increasing shear thinning, i.e. increasing $\alpha$.

For the second polymer solution, which exhibits normal stress effects but no shear thinning, we also found a power-law behaviour of the radius versus time. The fits to the data for $R(t)$ yield a spreading exponent close to but slightly smaller than 0.1 (figure 3*b*), very similar to Tanner's law. However, the prefactor is not simply given by the viscosity, as will be shown below.

## 3. Theory

### 3.1. *Power-law vicosity*

We consider here the dynamics of a thin layer of a fluid of surface tension $\sigma$ spreading on a horizontal hydrophilic substrate. In the corresponding lubrication theory, the only important component of the deformation rate tensor is the horizontal shear rate $\dot{\gamma}$, so that we assume a power-law viscosity $\eta = a\dot{\gamma}^{-\alpha}$. Considering cylindrical symmetry, let $h(t, r)$ be the film thickness as a function of time and of the radial coordinate. The lubrication equation has been derived by several authors (see e.g. King 2001*a*; Starov *et al.* 2003):

$$\frac{\partial h}{\partial t} + \nabla \cdot \left( \frac{1-\alpha}{3-2\alpha} \left( \frac{\sigma}{a} \nabla \cdot \nabla^2 h \right)^{\frac{1}{1-\alpha}} h^{\frac{3-2\alpha}{1-\alpha}} \right) = 0. \tag{3.1}$$

We have neglected gravity, assuming that the typical horizontal scale is smaller than the capillary length $\sqrt{\sigma/\rho g} \simeq 2.7$ mm. This is only approximately true in some experiments but it is sufficient to account for most of our observations. Using a time scale $\tau$ and a length scale $\ell$, one can look for self-similar solutions (King 2001*a*; Starov *et al.* 2003)

$$h(r, t) = \left( \frac{t}{\tau} \right)^{-2\frac{1-\alpha}{10-3\alpha}} \ell H \left( \frac{r}{\ell} \left( \frac{\tau}{t} \right)^{\frac{1-\alpha}{10-3\alpha}} \right). \tag{3.2}$$

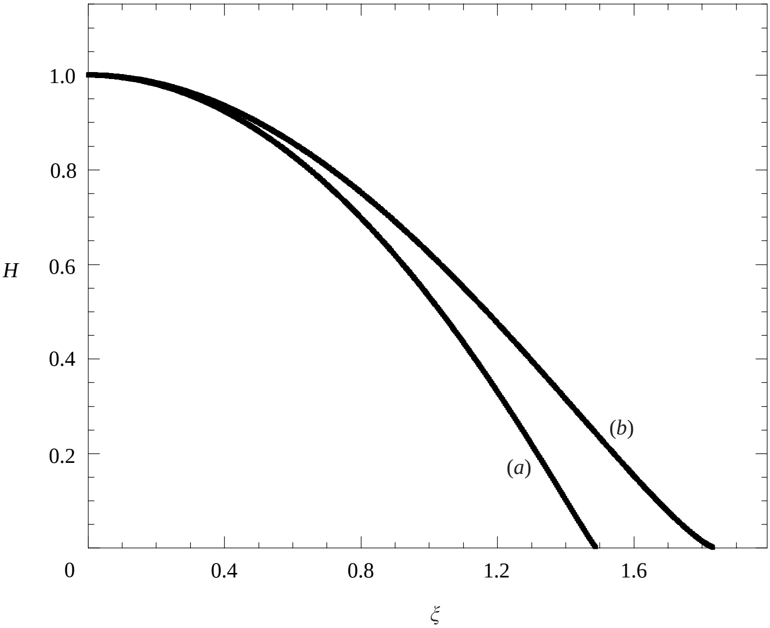

FIGURE 5. Two drop profiles $H(\xi)$ as given by (3.3) for (*a*) $\alpha = 0.2$ and (*b*) $\alpha = 0.8$.

The scaling law for the drop radius $R \sim t^n = t^{(1-\alpha)/(10-3\alpha)}$ can be compared directly to the results of the experiments; it is in fair agreement with the measurements (figure 4*a*).

To push the comparison between theory and experiment somewhat farther, we also calculate the prefactor. Consider the equation for the similarity function $H(\xi)$:

$$H''' + H''/\xi - H'/\xi^2 = n^{1-\alpha}\xi^{1-\alpha}/H^{2-\alpha}. \tag{3.3}$$

This equation has only one solution satisfying $H(0) = 1$ (choice of length scale), $H'(0) = 0$ (axisymmetry) and $H(\xi_c) = H'(\xi_c) = 0$ for some $\xi_c$ (zero contact angle at the drop boundary) (figure 5). A shooting method allows the numerical solution of this equation and gives the value of the non-dimensional drop radius $\xi_c$ and non-dimensional volume $\omega$. Coming back to dimensional units, this yields the prefactor of the drop radius scaling law

$$R = C\left(\frac{\sigma t^{1-\alpha}}{a}\right)^{\frac{1}{10-3\alpha}} \Omega^{\frac{3-\alpha}{10-3\alpha}}, \quad C = \xi_c\left(\left(\frac{1-\alpha}{3-2\alpha}\right)^{1-\alpha}\omega^{-3+\alpha}\right)^{\frac{1}{10-3\alpha}}. \tag{3.4}$$

Here $\Omega$ is the drop volume, $\sigma$ is again the surface tension and $a$ is the rheological prefactor in the shear-thinning law. The prefactor $C$ computed this way is not far from the measured one as shown in figure 4(*b*).

### 3.2. *Normal stress effects*

We now consider a fluid of surface tension $\sigma$, constant shear viscosity $\eta$ but normal stresses given by $N_1 = \psi_1\dot{\gamma}^2$. The quadratic dependence on the shear rate is an exact result for small elasticity, and describes the rheology data well. The normal stresses act in a similar way to the capillary pressure in driving the flow. Their contribution to the total pressure gradient can be estimated as $N_1 \sim \psi_1(\dot{R}/h)^2$, $\dot{R}$ being the contact

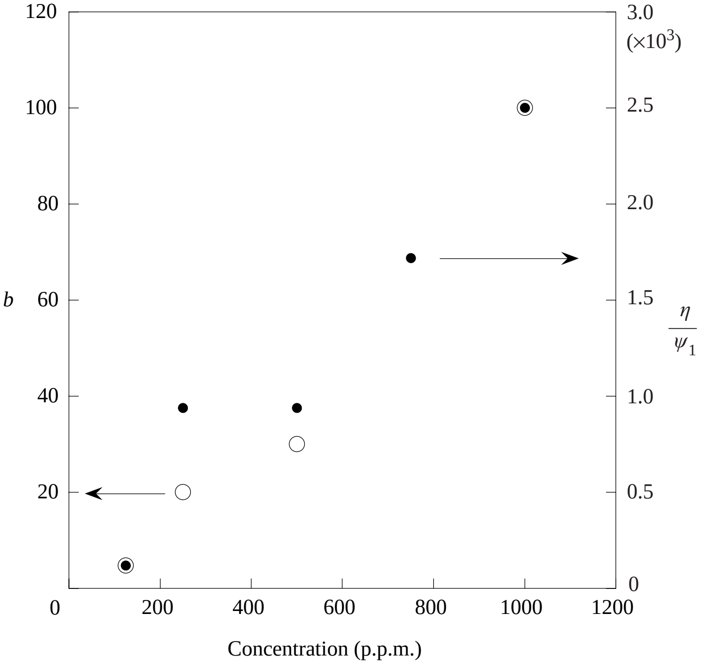

FIGURE 6. Factor $b$ deduced from figure 3($b$) versus concentration and comparison with the inverse of the relaxation time $\eta/\psi_1$ (see equation (3.6)).

line velocity and $h$ the typical drop height. If $X$ is the distance to the drop periphery, the normal stress gradient $\nabla N_1 \sim N_1/X$ drives the flow there.

To estimate the importance of this normal stress gradient, it must be compared to the viscous stress gradient $\eta \dot{R}/h^2$. Their ratio defines the rheological number

$$\mathscr{N} = \frac{\psi_1 \dot{R}}{\eta X}. \tag{3.5}$$

Near the drop centre, $\mathscr{N}$ is of the order of $\psi_1 \dot{R}/(\eta R) \sim \psi_1/(\eta t) \sim 10^{-2}$ for typical parameters, assuming a power-law dependence on time for $R$. The rheological number becomes of order unity at a small distance $X_c \sim \psi_1 \dot{R}/\eta$ from the three-phase contact line. Therefore, normal stresses are unimportant near the centre and for most of the flow the polymer solution behaves as a Newtonian liquid. Very close to the contact line, however, the outward flow is accelerated by the normal stress effect. The distance $X_c$ at which the normal stresses start to dominate the viscous stresses will act as a cut-off for the Cox–Voinov law for the contact angle (Cox 1986), $\theta^3 \sim \log(R/X_c)\eta \dot{R}/\sigma$. Using volume conservation $\Omega \sim \theta R^3$, this yields

$$R \sim \Omega^{3/10} \left(\frac{\sigma t}{\eta}\right)^{1/10} \left(\log \frac{\eta t}{10\psi_1}\right)^{-1/10}. \tag{3.6}$$

This can again be compared directly to the data. The experimental exponents are slightly smaller than 1/10 because of the logarithmic correction to the power-law behaviour. This correction is very difficult to observe with Newtonian liquids whereas it is evident here when fitting experimental data for the radius to the form $R = a(t/\log(bt))^{1/10}$. We find good agreement with equation (3.6), and in particular $b \simeq 0.04\eta/\psi_1$ (figure 6). We see that, even though the normal stresses are important only at the drop edge, this has a macroscopic consequence for the behaviour of the radius.

## 4. Discussion

The main and perhaps surprising conclusion of this work is that Tanner's law $R(t) \sim \Omega^{3/10}(\sigma/\eta)^{1/10}t^{1/10}$ is remarkably robust. Neither strong shear thinning, nor large normal stress effects lead to a very different spreading.

For shear-thinning fluids, this is surprising since calculations show that the contact-line singularity disappears. Roughly speaking, in the calculation this happens because the shear rate diverges near the contact line and therefore the viscosity tends to zero so that the dissipation does not diverge. In reality, of course, the viscosity will not go to zero, but rather to that of the solvent. This poses the question of the validity of a power-law viscosity for the fluids that we have used. Rheological data show that the solvent viscosity is reached at shear rates of the order of $\gamma \sim 10^4\ \mathrm{s}^{-1}$. The shear rate near the contact line is of the order of $\omega \sim v/h$, the typical velocity being $v \sim 10^{-3}\,\mathrm{m\,s}^{-1}$, so that the thickness $h$ at which the solvent viscosity is reached is $h \sim 100\,\mathrm{nm}$, comparable to the range of Van der Waals forces. We therefore conclude that the solvent viscosity does not matter, and that the results of the theory may be compared to the experiments.

For practical purposes, to predict the spreading rate of a slightly shear-thinning fluid, one can replace the viscosity with an effective viscosity $\eta_{\mathrm{eff}} = a\tau^{\alpha}$, where $\tau \sim \eta_{\mathrm{eff}} R_0/(\sigma\theta_0^3)$ is a typical experimental spreading time for an initial radius $R_0$ and contact angle $\theta_0$, so that

$$\eta_{\mathrm{eff}} = \left(\frac{R_0^{\alpha} a}{\sigma^{\alpha}\theta_0^{3\alpha}}\right)^{\frac{1}{1-\alpha}}. \tag{4.1}$$

For a fluid with normal stress effects that are not too large, one can proceed similarly using

$$\eta_{\mathrm{eff}} = \eta\left(\log\left(\frac{R_0\eta^2}{\psi_1\sigma\ \theta_0^3}\right)\right)^{1/10}. \tag{4.2}$$

It follows that for the spreading of non-Newtonian liquids new mechanisms operate that limit the speed of a contact line. In both cases, microscopic forces (i.e. van der Waals forces) appear to be unimportant. For a shear-thinning fluid, the contact line singularity is removed due to the viscosity decrease. On the other hand, normal stresses provide an additional driving force that overcomes the viscous resistance near the contact line. One would thus imagine that both shear thinning and normal stress effects should accelerate the motion of the contact line. In contrast with this naïve expectation, in both experiments the spreading is slowed down. This can be understood as follows. Both effects accelerate the flow near the contact line, and both effects do so more strongly as the shear rate is increased. Because the shear rate increases upon approaching the contact line, the parts closest to the corner will move faster, and the apparent contact angle decreases. Since the spreading velocity varies with the contact angle, the lowering of the contact angle decreases the driving force for spreading, and the contact line is slowed down, in agreement with the experimental observations.

A.B. is grateful to Martine Ben Amar for fruitful discussions. LPS de l'ENS is UMR 8550 of the CNRS associated with the Universities Paris 6 and Paris 7.

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