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Non-Newtonian thin films with normal stresses: dynamics and spreading

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Abstract. The dynamics of a thin film on a horizontal solid substrate is investigated in the case of non-Newtonian fluids exhibiting normal stress differences, the rheology of which is strongly non-linear. Two coupled equations of evolution for the thickness of the film and the shear rate are proposed within the lubrication approximation. This framework is applied to the motion of an advancing contact line. The apparent dynamic contact angle is found to depend logarithmically on a lengthscale determined solely by the rheological properties of the fluid and the velocity of the contact line.

PACS. 68.15.+e Liquid thin films – 83.60.Hc Normal stress differences and their effects (e.g. rod climbing) – 47.55.np Contact lines

Rapid Note

The spreading of a thin fluid layer on a substrate has received much attention due to its practical importance. However, the motion of a contact line is still a matter of debate (see Refs. [1–4] for a review). Macroscopically, there is a balance between viscous forces (shear viscosity μ) and capillary forces (surface tension σ). This results in the Cox-Voinov law [5], which relates the apparent (or dynamic) contact angle θ_d to the velocity U of the contact line

$$\theta_\mathrm{d}^3 = 9\frac{\mu U}{\gamma}\ln(x/\ell_m), \qquad (1)$$

x being the distance to the contact line. This equation is ill-defined for small x which reflects the divergence of the viscous stresses at the contact-line [6]. The value of the length ℓ_m depends on the regularising microscopic physics accounted for in the model — e.g. Van der Waals forces [7], slip [6] or diffuse interface [3] — so that macroscopic measurements can be used to probe microscopic properties. Experiments on the spreading of silicon oils [8] confirm the model based on Van der Waals forces [2]. However it is plausible that the relevant model depends on the nature of both the fluid and the substrate.

In applications, most fluids are complex and exhibit non-Newtonian properties. Except for some viscoelastic fluids [9], they have a nonlinear constitutive equation, which raises a theoretical challenge [10]. Until now, lubrication theories were restricted to fluids with no normal stresses, such as yield-stress fluids [11] or shear-thinning fluids [12–19]. Shear-thinning was even proposed as the regularising microscopical mechanism [20–22]. Experimental studies are fewer [23,24,18]; the more recent one [18] also considered fluids for which the only non-Newtonian property is the existence of normal stresses, for which no theoretical framework was available.

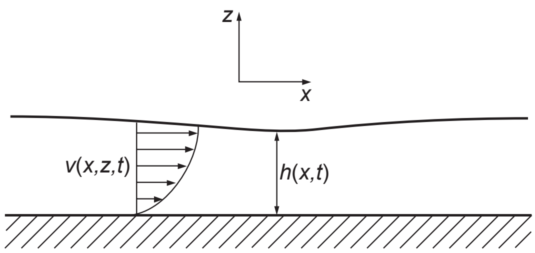

Fig. 1. Schematic of the geometry, defining the directions x, z, the film thickness h and horizontal velocity v.

In this Note we consider the spreading of a thin layer of fluid having a constant shear viscosity μ and exhibiting first normal stresses difference [25] $\sigma_{xx} - \sigma_{zz} = \psi(\partial_z v)^2$, σ being the stress tensor (see Fig. 1 for the geometry and other notations). In dilute polymeric suspensions, the second normal stress difference $\sigma_{yy} - \sigma_{zz}$ is negligible and the normal stress coefficient ψ can be considered as constant [25]. Within the lubrication approximation, we propose a set of two coupled equations of evolution (Eqs. (11, 12)) for the film height and the shear rate (averaged over the thickness). Then we investigate an advancing contact line (at velocity U). In particular we determine the lengthscale which replaces the microscopic length in (1),

$$\ell_m = \frac{\psi U}{b\mu}, \qquad (2)$$

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b being a numerical constant. The effect of normal stresses turns out to be close to that of van der Waals forces [7]: the shear rate is large at the film edge, so that the normal forces push the surface of the film and the substrate apart, which results in a precursor thin film driving the spreading.

As discussed at the end, the Cox-Voinov law with the the lengthscale ℓ_m defined in (2) leads to a visible logarithmic dependence in the radius of spreading droplets of a liquid exhibiting normal stresses, $R \sim t^{1/10}(\ln(\mu t/\psi))^{-1/10}$. The presence of the relaxation time $\tau = \psi/\mu$ of the fluid is in quantitative agreement with the experiments of [18] performed with polymeric solutions having various values of τ.

In view of the lubrication approximation, we introduce the aspect ratio $\epsilon = Z/X$ of the film, Z being a typical thickness and X the horizontal lengthscale. Let p be the pressure field and ϕ the potential of an applied body force such as a microscopic force or gravity (then $\phi = \rho g z$, ρ being the volumic mass). The stress balance reads

$$\partial_x \sigma_{xx} + \partial_z \sigma_{zx} = \partial_x \phi + \partial_x p \tag{3}$$

$$\partial_x \sigma_{xz} + \partial_z \sigma_{zz} = \partial_z \phi + \partial_z p. \tag{4}$$

As $\partial_x/\partial_z \sim \epsilon \ll 1$, equation (4) yields at the lower order in ϵ that $\pi = p + \phi - \sigma_{zz}$ is a function of x only. Then equation (3) becomes $\partial_x(\sigma_{xx} - \sigma_{zz}) + \partial_z \sigma_{zx} = \partial_x \pi$, i.e. , using the rheology,

$$\mu \partial_{zz} v + \psi\, \partial_x \left[(\partial_z v)^2\right] = \partial_x \pi \tag{5}$$

for $0 < z < h(x,t)$, and π is determined using the normal stress balance $-p + \sigma_{zz} = \gamma\kappa$ at the free surface, accounting for its surface tension γ and curvature κ, so that

$$\pi = -\gamma \partial_{xx} h + \phi(z = h). \tag{6}$$

The set (5, 6) is closed with mass conservation

$$\partial_t h + \partial_x \int_0^h v(z,t)\mathrm{d}z = 0. \tag{7}$$

Thus we obtain a system of PDEs for h and v. In fact, equation (5) can be solved for v by a series of the form

$$v(x,z,t) = \Sigma_{n=0}^{\infty}\, a_n(x) z^n, \tag{8}$$

where $a_0 = 0$ to ensure no slip at the substrate, $a_1(x,t) = 2s(x,t)$ is proportional to the mean shear rate across the thickness, $a_2 = \partial_x(-\pi + 4\psi s^2)/\mu$, and each following a_n can be computed recursively with the x-derivatives of the previous coefficients. Here we propose to truncate the expansion at order 2: $v = 2sz + a_2 z^2$, which corresponds to truncating equation (5) at order zero in z. Then the condition of no shear stress at the free surface $\partial_z v = 0$ yields $a_2 = -s/h$. The left-hand side of equation (5) becomes $2a_2 + \psi\partial_x((2s)^2)$ (at order 0 in z). As a consequence equations (5–7) reduce to two coupled PDEs for the thickness h and the mean shear rate s,

$$2\mu s + h\,\partial_x\left(\pi - 4\psi s^2\right) = 0, \tag{9}$$

$$\partial_t h + \frac{2}{3}\partial_x\left(h^2 s\right) = 0. \tag{10}$$

This set is readily generalised to account for a third direction y; $\mathbf{s} = (s_x, s_y)$ is then the vectorial horizontal mean shear:

$$2\mu \mathbf{s} + h\,\nabla\left(\pi - 4\psi \mathbf{s}^2\right) = 0, \tag{11}$$

$$\partial_t h + \frac{2}{3}\nabla\cdot\left(h^2 \mathbf{s}\right) = 0, \tag{12}$$

where the dynamic pressure is defined by

$$\pi = -\gamma \nabla^2 h + \phi(z = h) \tag{13}$$

and $\nabla = (\partial_x, \partial_y)$.

Now we proceed to the study of a moving contact line, the only driving forces being the capillary forces: $\pi = -\gamma\partial_{xx} h$. We consider a contact line advancing at constant velocity U towards $x = -\infty$, i.e. $h(x,t) = h(x+Ut)$ and $s(x,t) = s(x+Ut)$, so that equation (10) reads $U + 2/3\; hs = 0$. Replacing s in 10 yields

$$1 + \frac{1}{3\mathcal{C}} h^2 h''' - 6\ell \frac{h'}{h} = 0, \tag{14}$$

where $\mathcal{C} = \mu U/\gamma$ is the capillary number and $\ell = \psi U/\mu$ is the normal stress characteristic length. The scaling form of the solutions to (14) is

$$x = X\ell, \quad h(x) = \mathcal{C}^{1/3}\ell\, H(X), \tag{15}$$

which yields

$$1 + \frac{1}{3} H^2 H''' - 6\frac{H'}{H} = 0. \tag{16}$$

There is a continuum of solutions of equation (16) which vanish at $X = 0$ and have no macroscopic curvature, i.e. $H'' \to 0$ when $X \to +\infty$; they have the local behavior $H(X) \sim X^{2/3}$ near $X = 0$. The structure of the problem appears to be similar to that of the case of Van de Waals microscopic forces [7] (there the last term in the equation is H'/H^2). Following the same lines as in [7], we look for solutions of (16) which vanish for $X \to -\infty$ and have no macroscopic curvature. In the case of very strong normal stresses, equation (14) becomes $1 - 6\ell h'/h = 0$ so that we obtain the 'precursor' profile $h(x) = \alpha \exp(x/6\ell)$, which plays the same role as the 'maximal film' solution of [7]. The full equation (16) has a solution with the same asymptotics $H_0(X) = \exp(X/6) + O(\exp(2X/3))$ for $X \to -\infty$. Linearising equation (16) around H_0 and solving the linear ODE obtained yields

$$H(X) \simeq H_0(X) + aH_0'(X) + bH_+(X) + cH_-(X). \tag{17}$$

The appearance of H_0' corresponds to the invariance by translation of equation (16): one can choose $a = 0$ to set the origin. $H_\pm$ can be expressed using hypergeometric functions and have the leading asymptotics

$$H \pm (X) \sim \exp(7X/24)\exp(\pm 12\sqrt{2}\exp(-X/4))$$

for $X \to -\infty$. We set $b = 0$ as H_+ is unbounded. We look for solutions having the asymptotic form (17) for

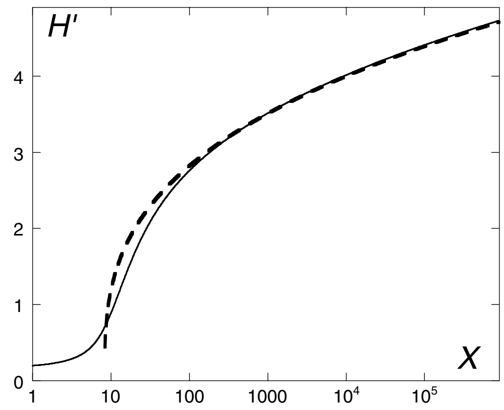

Fig. 2. Film slope for an advancing contact line as given by the solution to (16): slope $H'(X)$ (continuous line) and comparison with the asymptotic form $(9\ln(\beta X))^{1/3}$ with $\beta = 0.12$ (dashed line).

$X \to -\infty$ and we shoot on the value of c to get $H'' \to 0$ for $X \to \infty$. We find only one such solution ($c \simeq -0.1$). It has the classical asymptotic form $H = 3^{2/3} X[\ln(\beta X)]^{1/3}$, with $\beta = 0.12$. This solution is depicted in Figure 2 and allows a matching between Cox-Voinov's law (1) and the strong normal stress asymptotics $H_0(X) \sim \exp(X/6)$ for $X \to -\infty$.

To summarise, we proposed the set (11, 12) of coupled PDEs for the film thickness and mean shear. It was obtained using a truncation of the expansion of the solution to the equilibrium equations. Direct comparison with the experiments might require an adjustment of the prefactor of ψ in equation (11); for instance the averaging of equation (5) would yield a prefactor 4/3 instead of 4. Within this framework, we showed that the rheology provides a regularising lengthscale ℓ_m (Eq. (2)) associated with a precursor film.

This result can be directly applied to the case of spreading droplets as investigated experimentally in [18]. The velocity of the contact line $U = \dot{R}$ is the derivative of the drop radius R with respect to time t. The dynamic contact angle θ_d (Eq. (1)) can be evaluated at $x \sim R$. Using conservation of the drop volume $\Omega \sim R^3\theta_\mathrm{d}$, one finds

$$R \sim \Omega^{3/10} \left(\frac{\gamma t}{\mu}\right)^{1/10} \left(\ln \frac{\mu t}{\psi}\right)^{-1/10}. \qquad (18)$$

This logarithmic dependence on the relaxation time $\tau = \psi/\mu$ of the polymeric solution is in agreement with the measurements [18]. Actually, the spreading is slowed down, as explained in the conclusion of [18]. In those experiments, τ increased from 0.4 ms to 10 ms when increasing the concentration of polymer, while the typical spreading velocity U decreased from 0.1 to 0.2 mm/s, so that the regularising lengthscale ℓ_m is of the order of $U\tau \sim 1\ \mu$m.

Obviously the results are valid as long as ℓ_m is much larger than any microscopic length such as a slip length or the size of a precursor film. The other limitation is that the asymptotic behavior for the Cox-Voinov law (1) is attained when $x \simeq 100\ell$ (Fig. 2) or about 0.1 mm in experiments, which is comparable to the scale at which gravity becomes important (see e.g. [4] for a discussion of this matter). For a closer comparison of our results with experiments, gravity should be included. The present study could be improved by a truncation at higher order, although the robust asymptotics in the 'precursor' and far from the 'contact line' would not be altered; however this would yield a formidable numerical task as the order of the PDEs would increase with the order of the truncation. Another extension would be to match the region where normal stresses balance capillarity to the smaller region where microscopic physics becomes important.

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