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Slip vs. viscoelasticity in dewetting thin films

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Abstract. Ultrathin polymer films on non-wettable substrates display dynamic features which have been attributed to either viscoelastic or slip effects. Here we show that in the weak- and strong-slip regime, effects of viscoelastic relaxation are either absent or essentially indistinguishable from slip effects. Strong slip modifies the fastest unstable mode in a rupturing thin film, which questions the standard approach to reconstruct the effective interface potential from dewetting experiments.

PACS. 83.60.Bc Linear viscoelatiscity – 47.50.-d Non-Newtonian fluid flows – 68.15.+e Liquid thin films

Introduction

In recent years it has been shown that the physics of polymeric thin films on non-wettable surfaces can be described, to an astonishing level of detail, by lubrication models derived from the Navier-Stokes equation for simple liquids [1, 2]. However, ultrathin dewetting films exhibit unusual features in their rupture dynamics which show up in the morphology and velocities of dewetting holes [3]. It has been suggested that viscoelasticity plays an important role in these films, in particular when the polymer length scales become comparable to the film thickness. There is now a large number of modelling attempts to explain these features [4–8]. Most of them assume a generalized Maxwell- or Jeffreys-type dynamics for the stress-strain relation in these films, sometimes in combination with additional flow functions; all these assumptions are, while not entirely artificial, hard to solidly justify at present. The earlier work of Safran and Klein also included an explicit zero-frequency shear modulus or elasticity [9]. Here we are exclusively concerned with liquid-polymer films and, in the absence of better knowledge, we believe that the Jeffreys model remains a useful starting point for modeling, with the idea to later confront the predictions with experiment.

As has been shown very recently, thin-film lubrication models can be classified into different slip classes, and separate models have to be derived for each class. There are models valid specifically in the limit of strong slip [10,11] but also in intermediate slip regimes [11]. The distinction of different slip classes is essential for the description of dewetting experiments of PS-films on substrates with different slip properties [12]. This last result has shown that slip effects can indeed explain the anomalies in the shape of dewetting films.

As we demonstrate here, the distinction of different slip classes remains true for viscoelastic thin films of Jeffreys type. We show that it is easy to generalize the recently proposed lubrication model for Newtonian liquids in the strong-slip regime [10,11] to a Jeffreys model. We here apply this model, as well as the recently developed model for the weak-slip case [13], to determine the onset conditions of rupture in unstable thin films.

Model assumptions and lubrication equations

We begin with the bulk dynamic equations for the viscoelastic liquid. It is assumed as incompressible, hence the velocity field $\mathbf{u} = (u_x, u_y, u_z)$ fulfills the mass conservation equation

$$\boldsymbol{\nabla} \cdot \mathbf{u} = 0\,. \tag{1}$$

The equation of momentum conservation is given by

$$\varrho \frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} = -\boldsymbol{\nabla} p_R + \boldsymbol{\nabla} \cdot \boldsymbol{\tau} \tag{2}$$

where $p_R = p + V'$ is the augmented pressure, with p as capillary pressure and $-V'$ as disjoining pressure due to van der Waals-type dispersion forces. The traceless part

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of the stress tensor is described by a symmetric matrix $\boldsymbol{\tau}$. Further, in equation (2), $\mathrm{d}/\mathrm{d}t$ is the total derivative, and $\boldsymbol{\nabla}$ abbreviates the partial derivative vector with entries ∂_i, $i = x, y, z$.

To complete the model we have to choose a constitutive relation for the stress tensor $\boldsymbol{\tau}$. As argued in the introduction, we opt for the linear Jeffreys model defined by

$$(1 + \lambda_1\partial_t)\boldsymbol{\tau} = \eta(1 + \lambda_2\partial_t)\dot{\boldsymbol{\gamma}} \tag{3}$$

in which $\dot{\boldsymbol{\gamma}}$ is the strain rate, $\dot{\gamma}_{ij} = \partial_i u_j + \partial_j u_i$. The rates $\lambda_1 > \lambda_2$ govern the relaxation of the stress and strain rate, respectively.

In order to derive the equations for a thin film of height $z = h(x, y, t)$ we have, for the incompressible case, the kinematic condition

$$\partial_t h = -\nabla_\parallel \cdot \int_0^h \mathrm{d}z\ \mathbf{u}_\parallel \tag{4}$$

where $\nabla_\parallel = (\partial_x, \partial_y)$, and $\mathbf{u}_\parallel = (u_x, u_y)$. The boundary conditions at the free surface correspond to the vanishing of the stress tensor components tangential to the film surface (*i.e.*, we neglect the vapor phase), while the normal component of the stress tensor obeys

$$(\boldsymbol{\tau} - p_R\mathbf{1}) \cdot \mathbf{n} = 2\sigma\kappa\mathbf{n}\,, \tag{5}$$

where σ is the surface tension of the film, $\mathbf{1}$ a 3×3 unit matrix, and κ the local mean curvature with sign convention that $\kappa < 0$ for a spherical drop. Finally, in equation (5), the normal vector to the film is given by $\mathbf{n} = (-\nabla_\parallel h, 1)/\sqrt{g}$, with $g = 1 + (\nabla_\parallel h)^2$. The model is completed by the boundary conditions at the substrate which are of Navier type, *i.e.*,

$$u_z = 0\,, \qquad u_i = \frac{b}{\eta}\tau_{iz}\,, \tag{6}$$

where b is the slip length.

We now sketch the derivation of the lubrication model for strong and weak slip that can be derived from this bulk dynamics; for the technical details we refer the readers to references [11,13] and Appendix A to this paper.

The basis of the lubrication approach is the introduction of a relative scale of the thin-film height to its lateral extension. Denoting the direction of the film height by z and the lateral extension by the two-dimensional vector (x, y), we introduce the scale H in the direction of the film height and L in the lateral direction. Thus, we have

$$z = Hz^* \quad (x, y) = (Lx^*, Ly^*)\,, \qquad b = Hb^*. \tag{7}$$

We then define

$$\epsilon \equiv \frac{H}{L} \ll 1 \tag{8}$$

as our (small) scaling parameter which will serve to control the different orders of the approximation. Further, time is scaled by $T = L/U$, where U is the corresponding velocity scale. The stress tensor scales as

$$\tau_{ij} = \frac{\eta}{T}\tau^*_{ij} \tag{9}$$

for $(i, j) = (x, y)$ and, additionally, $i = j$. The remaining components scale as

$$\tau_{ij} = \frac{\eta}{\epsilon T}\tau_{ij}\,. \tag{10}$$

The distinction between weak- and strong-slip lengths arises from the choice of balancing conditions between the forces acting on the film. In the weak-slip limit, one has with the pressure scale P [13]

$$\frac{PH}{\eta U} \sim \epsilon^{-1}\,, \tag{11}$$

while in the strong-slip limit we need [11]

$$\frac{PH}{\eta U} \sim \epsilon\,. \tag{12}$$

The Reynolds number $Re = \varrho UL/\eta$ now scales as either

$$Re = \epsilon^3 Re^* \tag{13}$$

in the weak-slip case, or as

$$Re = \epsilon Re^* \tag{14}$$

in the strong-slip case, where Re^* is the reduced Reynolds number of order unity. In the weak-slip regime the non-dimensional slip length $b = O(1)$ —*i.e.*, it has no dependence on ϵ, while in the strong-slip regime, the dependence is $b* = O(1/\epsilon^2)$ which is made explicit by the definition

$$b* \equiv \frac{\beta_s}{\epsilon^2}\,, \tag{15}$$

where β_s is a constant.

We now first state the result for the strong-slip case, details are given in Appendix A. Being interested here only in the conditions of thin-film rupture, we restrict the discussion to the (laterally) one-dimensional case; the extension to the full two-dimensional case is straightforward.

In the strong-slip lubrication limit one ends up with the following system of equations (we put $\sigma = 1$):

$$\begin{aligned} hRe^*(\partial_t u + u\partial_x u) &= h\partial_x[\partial_x^2 h - V'(h)] + \partial_x(4hq) - \frac{u}{\beta_s}\,, \\ (1 + \lambda_1\partial_t)q &= (1 + \lambda_2\partial_t)\partial_x u\,, \\ \partial_t h + \partial_x(hu) &= 0\,, \end{aligned} \tag{16}$$

where q is related to the stress tensor, see Appendix A. Note that the system (16) readily reduces to the Newtonian case if $\lambda_1 = \lambda_2 = 0$; the added complexity of the viscoelasticity is thus relatively minor in this limit.

By contrast, in the weak-slip limit, one is able to derive the equation [13]

$$\begin{aligned} &(1 + \lambda_2\partial_t)\partial_t h + (\lambda_2 - \lambda_1)\partial_x\left(\frac{h^2}{2}Q - hR\right)\partial_t h = \\ &-\partial_x\left[\left((1+\lambda_1\partial_t)\frac{h^3}{3} + (1+\lambda_2\partial_t)bh^2\right)\partial_x(\partial_x^2 h - V'(h))\right]\,, \end{aligned} \tag{17}$$

where the two functions Q and R fulfill the differential equations

$$(1+\lambda_2\partial_t)Q = -\partial_x(\partial_x^2 h - V'(h)) \tag{18}$$

and

$$(1+\lambda_2\partial_t)R = -h\partial_x(\partial_x^2 h - V'(h))\,. \tag{19}$$

Note that for $\lambda_2 \to 0$, equation (17) collapses to a single equation; this limit corresponds to the simplest Maxwell model. In the case $\lambda_1 = \lambda_2$ one recovers the thin-film equation of the Newtonian liquid with an extra multiplicative factor $(1+\lambda_1\partial_t)$ on both sides.

Linear stability analysis

We now turn to the linear stability analysis of a thin film of thickness h_0 which experiences a dispersion force which destabilizes it (*i.e.*, $V''(h_0) < 0$). The two different cases yield:

A) *Weak slip.* The linear stability analysis is easily determined by assuming that one has up to first order, as indicated by the index, the relations

$$h = h_0 + \delta h_1\,, \qquad Q = \delta Q_1\,, \qquad R = \delta R_1, \tag{20}$$

where $0 < \delta \ll 1$ with, in addition,

$$(h_1(x,t), Q_1(x,t), R_1(x,t)) \equiv (\hat{h}_1, \hat{Q}_1, \hat{R}_1)e^{ikx+\omega t}\,. \tag{21}$$

Note that the zero-order contributions to Q and R vanish.

The resulting dispersion relation $\omega(k)$ can be expressed as

$$(1+\lambda_2\omega)\omega = \omega_N(1+\Lambda\,\omega)\,, \tag{22}$$

where

$$\omega_N(k) = \left(\frac{h_0^3}{3} + bh_0^2\right)\Omega(k) \tag{23}$$

with

$$\Omega(k) = -(k^4 + k^2 V''(h_0)) \tag{24}$$

is the dispersion relation of the Newtonian liquid. Finally, the (positive) parameter Λ appearing in equation (22) is given by

$$\Lambda \equiv \lambda_2 + \frac{(\lambda_1-\lambda_2)h_0^3}{h_0^3 + 3bh_0^2}\,. \tag{25}$$

From an analysis of equation (22) one finds two solution branches, one strictly negative and stable and one which has the same sign and zeroes as $\omega_N(k)$. Further, since the wave vector k does not appear explicitly in equation (22), also the fastest unstable mode is unaffected by viscoelastic relaxation. The instability of a weakly slipping Jeffreys film is therefore identical to that of the Newtonian film. In Appendix B we compare this finding to the results obtained earlier by Safran and Klein [9].

B) *Strong slip.* In complete analogy to case A) one puts

$$h = h_0 + \delta h_1\,, \qquad q = \delta q_1\,, \qquad u = \delta u_1 \tag{26}$$

and, with equation (21), one finds the dispersion relation

$$(1+\lambda_1\omega)(h_0 Re^*\omega + \beta_s^{-1})\omega + 4h_0k^2\omega(1+\lambda_2\omega) \\ -h_0^2\Omega(k)(1+\lambda_1\omega) = 0\,. \tag{27}$$

Again it is immediately evident that there exists a solution branch with the same zeros as $\Omega(k)$. This branch has the same sign as $\Omega(k)$, and the other branches are stable. The range of unstable modes is therefore unaffected by viscoelastic relaxation.

However, in contrast to the weak-slip case, the most unstable wave number k_m is modified and satisfies the case $Re^* = 0$ (which applies to the systems studied in [12]),

$$4\beta_s h_0^3 k_m^4 + h_0^2\left(2k_m^2 + V''(h_0)\right)\frac{1+\lambda_1\beta_s h_0^2 k_m^4}{1+\lambda_2\beta_s h_0^2 k_m^4} = 0. \tag{28}$$

This result shows that the most unstable mode is strongly affected by slip, as was already observed for the case of a Newtonian liquid [10]. In addition we find that k_m also depends on the relaxation parameters λ_1 and λ_2. In the limit $\lambda_1, \lambda_2 \gg 1$ or $\beta_s \gg 1$ equation (28) simplifies to

$$k_m^2 = -\frac{\rho}{4} + \sqrt{\frac{\rho^2}{16} - \frac{V''(h_0)\rho}{4}}, \qquad \rho = \frac{\lambda_1}{\beta_s h_0 \lambda_2}\,. \tag{29}$$

Note that the most unstable wavelength depends on the combination of systems lengths $\beta_s h_0$ and diverges for $\beta_s \to \infty$, in accordance with the Newtonian case studied in [10]. Note that this parameter combination plays a role in the characterisation of the different morphologies of the rims of holes in dewetting films [14,15]. Our result (29) also holds for $Re^* \neq 0$, but the condition corresponding to equation (28) is much more involved.

Conclusion

Based on the derivation of lubrication models for thin-film dynamics of Jeffreys type we conclude that both in the weak- and strong-slip limits, linear viscoelastistic effects are essentially absent for film rupture. By contrast, strong slip affects the most preferred wave number, which now also depends on the relaxation parameters. In particular, from equation (28) it appears that the standard approach for the reconstruction of the interface potential, which is based on the wavelength of the fastest-growing mode, is questionable for films subject to strong slip.

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Appendix A. Strong-slip lubrication limit for the Jeffreys model

The derivation of the strong-slip lubrication model for the linear Jeffreys case follows closely both the calculation in

the weak-slip regime, and the strong-slip Newtonian case. As in [11], the starting point is the ansatz

$$(u, w, h, p_R, \tau_{ij}) = (u_0, w_0, h_0, p_{R0}, \tau_{ij0}) + \epsilon^2(u_1, w_1, h_1, p_{R1}, \tau_{ij1}), \quad \text{(A.1)}$$

where u and w are the velocity field components in x- and z-directions, neglecting the transverse y-direction. To leading order we find the equations

$$\tau_{xz0} = 0\,, \quad \text{(A.2)}$$

$$(1 + \lambda_2\partial_t)\partial_z u_0 = 0 \quad \text{(A.3)}$$

with the solution

$$\partial_z u_0 = c(x, z)\exp(-t/\lambda_2)\,. \quad \text{(A.4)}$$

We select the solution $c \equiv 0$ since any other solution would correspond to a strong prestressing of the film at times $t \to -\infty$. Therefore, $u_0 = f(x, t)$, and from the mass conservation we have $\partial_x f = -\partial_z w_0$, hence $w_0 = -z\partial_x f$. It thus follows

$$(1 + \lambda_1\partial_t)\tau_{zz0} = -(1 + \lambda_2\partial_t)\partial_x f \quad \text{(A.5)}$$

which reads in integrated form as

$$\tau_{zz0} = -\frac{2}{\lambda_1}\int_{-\infty}^{t} \mathrm{d}t' e^{(t-t')/\lambda_1}(1 + \lambda_2\partial_t)\partial_x f = -\tau_{xx0}\,. \quad \text{(A.6)}$$

To solve for $f(x, t)$, we need to make use of the next order, which gives

$$Re^*(\partial_t + f\partial_x)f = \partial_x\tau_{xx0} + \partial_z\tau_{xz1} = -\partial_x p_{R0}\,, \quad \text{(A.7)}$$

where $p_{R0} = -\partial_{xx}h_0 - \tau_{zz0}$. This can be written as

$$Re^*(\partial_t + f\partial_x)f = \partial_z\tau_{xz1} + \partial_{xxx}h_0 + \frac{4}{\lambda_1}\partial_x\int_{-\infty}^{t} \mathrm{d}t' e^{(t-t')/\lambda_1}(1 + \lambda_2\partial_t)\partial_x f\,. \quad \text{(A.8)}$$

From the boundary condition at the free surface we find to second order

$$((\tau_{xx0} - \tau_{zz0}) + \tau_{xz0}(\partial_x h_0))(\partial_x h_0) = \tau_{xz1} \quad \text{(A.9)}$$

and hence

$$\tau_{xz1} = -2(\partial_x h_0)\tau_{zz0}\,. \quad \text{(A.10)}$$

It remains to determine the second-order result from the boundary condition at the substrate. We have $\tau_{xz1} = f/\beta$ and we can now integrate equation (A.8) with respect to z across the film from 0 to h_0 and obtain the system of equations given in the text (with $f \equiv u$), and where

$$q = -\frac{\tau_{zz0}}{2}\,. \quad \text{(A.11)}$$

Appendix B. Comparison to the dispersion relations obtained by Safran and Klein

The instability of thin viscoelastic films had been previously discussed by Safran and Klein [9]. These authors start from the relationship between the stress and rate-of-strain tensor given by

$$\tau(\omega) = \eta(\omega)\dot{\gamma}(\omega) \quad \text{(B.1)}$$

(the authors use ε instead of γ, which we avoid to not confuse with the lubrication parameter). For viscoelastic materials with a single relaxation time $\tau_r = 1/\omega_r$ they have

$$\eta(\omega) = \eta_\infty + \frac{E}{\omega + \omega_r}\,. \quad \text{(B.2)}$$

This expression is equivalent to our equation (3) provided one puts for η in our equation (3)

$$\eta = \eta_\infty\frac{\lambda_1}{\lambda_2} \quad \text{(B.3)}$$

and

$$\frac{1}{\lambda_1} = \omega_r\,, \qquad \frac{1}{\lambda_2} = \frac{E}{\eta_\infty} + \omega_r\,. \quad \text{(B.4)}$$

It is then apparent that the paper by Safran and Klein contains an error. While their dispersion relation equation (24),

$$\omega(q) = -\frac{a(q)}{2} \pm \frac{1}{2}\left[a^2(q) + 4b(q)\right]^{1/2} \quad \text{(B.5)}$$

is correct, the coefficients of this equation given in the subsequent equations (25) and (26) are not. The correct coefficients are

$$a(q) = \alpha q^2[q^2 - q_c^2] + \frac{E}{\eta_\infty} + \omega_r \quad \text{(B.6)}$$

and

$$b(q) = -\omega_r\alpha q^2[q^2 - q_c^2]\,, \quad \text{(B.7)}$$

in accord with our finding here. A comparison of this result with equation (19) in Safran and Klein confirms this, and shows that their eqs. (24-26) have the wrong zeros in wave vector. The error progresses on in their paper to equation (31).

As a final remark, we note that the elastic limit is obtained by letting $\omega_r \to 0$, which in our model corresponds to the (singular) limit $1/\lambda_1 \to 0$ with λ_1/λ_2 finite. The analysis shows that, as found by Klein and Safran, elastic behaviour at small wavelengths can stabilize the film. This also holds qualitatively for the strong-slip case.

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