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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.

1 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, 5, 6, 7, 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. In the absence of better knowledge, the Jeffreys-model therefore remains a useful starting point for modeling, with the idea to 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 [9, 10] but also in intermediate slip regimes [10]. The distinction of different slip classes is essential for the description of dewetting experiments of PS-films on substrates with different slip properties [11]. 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 [9, 10] to a Jeffreys model. We here apply this model, as well as the recently developed model for the weak slip case [12], to determine the onset conditions of rupture in unstable thin films.

2 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

$$\nabla \cdot \mathbf{u} = 0. \quad (1)$$

The equation of momentum conservation is given by

$$\rho \frac{d\mathbf{u}}{dt} = -\nabla p_R + \nabla \cdot \tau \quad (2)$$

where $p_R = p + V'$ is the augmented pressure, with p as capillary pressure and V' as the van der Waals-type dispersion forces. The traceless part of the stress tensor is described by a symmetric matrix τ . Further, in eq.(2), d/dt is the total derivative, and ∇ 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 τ . As argued in the introduction, we opt for the linear Jeffreys model defined by

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

in which $\dot{\gamma}$ is the strain rate, $\dot{\gamma}_{ij} = \partial_i u_j + \partial_j u_i$. The rates λ_1, λ_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

$$\partial_t h = -\nabla_{\parallel} \cdot \int_0^h dz \mathbf{u}_{\parallel} \quad (4)$$

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

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

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 eq.(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 surface which are of Navier type, i.e.,

$$u_z = 0, \quad u_i = \frac{b}{\eta} \tau_{iz} \quad (6)$$

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; the details can be found in refs. [12, 10], and in the Appendix to this paper.

First, we introduce a measure of the relative scale of the thin film height H , $z = Hz^*$, to its lateral extension, L , $(x, y) = L(x^*, y^*)$, and we define $\epsilon \equiv H/L \ll 1$. Time is scaled by $T = U/L$, where U is the velocity scale. The stress tensor scales as

$$\tau_{ij} = \frac{\eta}{T} \tau_{ij}^* \quad (7)$$

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

$$\tau_{ij} = \frac{\eta}{\epsilon T} \tau_{ij}^*. \quad (8)$$

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 [12]

$$\frac{PH}{\eta U} \sim \epsilon^{-1}, \quad (9)$$

while in the strong slip limit we need [10]

$$\frac{PH}{\eta U} \sim \epsilon. \quad (10)$$

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

$$Re = \epsilon^3 Re^* \quad (11)$$

in the weak slip case, or as

$$Re = \epsilon Re^* \quad (12)$$

in the strong slip case, where Re^* is the reduced Reynolds number of order one. Finally, the slip length b scales as $b = O(1)$ in the weak slip regime and $b = \beta_s \epsilon^{-2}$ in the strong slip case.

We first state the result for the strong slip case, details are given in the Appendix. 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 $\sigma = 1$),

$$\begin{aligned} hRe^*(\partial_t u + u\partial_x u) &= h\partial_x[\partial_x^2 h - V'(h)] + \partial_x(4hq) - \frac{u}{\beta_s}, \\ (1 + \lambda_1 \partial_t)q &= (1 + \lambda_2 \partial_t)\partial_x u, \end{aligned} \quad (13)$$

$$\partial_t h + \partial_x(hu) = 0.$$

where q is related to the stress tensor, see Appendix. Note that the system (13) 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 [12]

$$(1 + \lambda_2 \partial_t) \partial_t h + (\lambda_2 - \lambda_1) \partial_x \left(\frac{h^2}{2} Q - hR \right) \partial_t h = \quad (14)$$

$$- \partial_x \left[\left((1 + \lambda_1 \partial_t) \frac{h^3}{3} + (1 + \lambda_2 \partial_t) b h^2 \right) \partial_x (\partial_x^2 h - V'(h)) \right],$$

where

$$(1 + \lambda_2 \partial_t) Q = -\partial_x (\partial_x^2 h - V'(h)) \quad (15)$$

and

$$(1 + \lambda_2 \partial_t) R = -h \partial_x (\partial_x^2 h - V'(h)). \quad (16)$$

Note that for $\lambda_2 \rightarrow 0$, eq.(14) 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.

3 Linear stability analysis.

We now turn to the linear stability analysis of a thin film which experiences a dispersion forces 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

$$h = h_0 + \delta h_1, \quad Q = \delta Q_1, \quad R = \delta R_1, \quad (17)$$

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

$$(h_1(x, t), Q_1(x, t), R_1(x, t)) \equiv (\hat{h}_1, \hat{Q}_1, \hat{R}_1) e^{ikx + \omega t}. \quad (18)$$

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

$$(1 + \lambda_2 \omega) \omega = \omega_N (1 + \Lambda \omega) \quad (19)$$

where

$$\omega_N(k) = - \left(\frac{h_0^3}{3} + b h_0^2 \right) g(k) \quad (20)$$

with

$$g(k) = k^4 + k^2 V''(h_0) \quad (21)$$

is the dispersion relation of the Newtonian liquid, and

$$\Lambda \equiv \lambda_2 + \frac{(\lambda_1 - \lambda_2) h_0^3}{h_0^3 + 3b h_0^2} \quad (22)$$

From eq.(19) it is easy to see that the structure of the dispersion relation of the Jeffreys film is identical to that of the Newtonian film. The range of unstable modes is the interval between the two zeroes of eq.(19) which is given by the

two zeroes of $g(k)$. Further, also the fastest unstable mode is unaffected by viscoelastic relaxation.

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

$$h = h_0 + \delta h_1, \quad q = \delta q_1, \quad u = \delta u_1 \quad (23)$$

and, with eq.(18), one finds the dispersion relation

$$(1 + \lambda_1 \omega)(h_0 Re^* \omega + \beta_s^{-1}) \omega + 4h_0 k^2 \omega (1 + \lambda_2 \omega) + h_0^2 g(k) (1 + \lambda_1 \omega) = 0. \quad (24)$$

Again it is immediately evident that the range of unstable modes is unaffected by viscoelastic relaxation. The most unstable wavenumber k_m satisfies for the case $Re^* = 0$ which applies to the systems studied in [11]

$$4\beta_s h_0^3 k_m^4 + h_0^2 (2k_m^2 + V''(h_0)) \frac{1 + \lambda_1 \beta_s h_0^2 k_m^4}{1 + \lambda_2 \beta_s h_0^2 k_m^4} = 0. \quad (25)$$

This result shows that the most unstable mode is strongly affected by slip, as was already observed for the case of a Newtonian liquid [9]. In addition we find that k_m also depends on the relaxation parameters λ_1 and λ_2 . In the limit $\lambda_1, \lambda_2 \gg 1$ eq. (25) simplifies to

$$k_m^2 = -\frac{\rho}{4} \pm \sqrt{\frac{\rho^2}{16} - \frac{V''(h_0)\rho}{4}}, \quad \rho = \frac{\lambda_1}{\beta_s h_0 \lambda_2}. \quad (26)$$

This result also holds for $Re^* \neq 0$, but the condition corresponding to eq.(25) is much more involved.

4 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 viscoelastic effects are essentially absent for film rupture. By contrast, strong slip affects the the most preferred wavenumber, which now also depends on the relaxation parameters. In particular, from eq.(25) 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.

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 [10], the starting point is the ansatz

$$\begin{aligned} (u, w, h, p_R, \tau_{ij}) &= (u_0, w_0, h_0, p_{R0}, \tau_{ij0}) \\ &+ \epsilon^2(u_1, w_1, h_1, p_{R1}, \tau_{ij1}) \end{aligned} \quad (27)$$

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

$$\tau_{xz0} = 0 \quad (28)$$

$$(1 + \lambda_2 \partial_t) \partial_z u_0 = 0 \quad (29)$$

with the solution

$$\partial_z u_0 = c(x, z) \exp(-t/\lambda_2). \quad (30)$$

We select the solution $c \equiv 0$ since any other solution would correspond to a strong prestressing of the film at times $t \rightarrow -\infty$. 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

$$(1 + \lambda_1 \partial_t) \tau_{zz0} = -(1 + \lambda_2 \partial_t) \partial_x f. \quad (31)$$

which reads in integrated form as

$$\tau_{zz0} = -\frac{2}{\lambda_1} \int_{-\infty}^t dt' e^{(t-t')/\lambda_1} (1 + \lambda_2 \partial_t) \partial_x f = -\tau_{xx0}. \quad (32)$$

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

$$Re^*(\partial_t + f \partial_x) f = \partial_x \tau_{xx0} + \partial_z \tau_{xz1} = -\partial_x p_{R0} \quad (33)$$

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

$$\begin{aligned} Re^*(\partial_t + f \partial_x) f &= \partial_z \tau_{xz1} + \partial_{xxx} h_0 \\ &+ \frac{4}{\lambda_1} \partial_x \int_{-\infty}^t dt' e^{(t-t')/\lambda_1} (1 + \lambda_2 \partial_t) \partial_x f \end{aligned} \quad (34)$$

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

$$((\tau_{xx0} - \tau_{zz0}) + \tau_{xz0}(\partial_x h_0))(\partial_x h_0) = \tau_{xz1} \quad (35)$$

and hence

$$\tau_{xz1} = -2(\partial_x h_0) \tau_{zz0}. \quad (36)$$

It remains to determine the second order result from boundary condition at the substrate. We have $\tau_{xz1} = f/\beta$ and can now integrate eq.(34) with respect to z across the film from 0 to h_0 and obtain the system of eqs. given in the text (with $f \equiv u$), and where

$$q = -\frac{\tau_{zz0}}{2}. \quad (37)$$

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