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A thin-film equation for viscoelastic liquids of Jeffreys type

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Abstract

We derive a novel thin film equation for linear viscoelastic media describable by generalized Maxwell or Jeffreys models. As a first application of this equation we discuss the shape of a liquid rim near a dewetting front. Although the dynamics of the liquid is equivalent to that of a phenomenological model recently proposed by Herminghaus et al. [19], the liquid rim profile in our model always shows oscillatory behaviour, contrary to that obtained in the former. Our finding supports recent conclusions, based on calculations for Newtonian liquids, that the monotonely decaying rim profiles are a consequence of large slip effects in thin polymer films.

1 Introduction

The understanding of the dynamics and in particular the stability of thin polymeric films on substrates has advanced considerably in recent years [1, 2]. This achievement is to a large part the result of the development of novel experimental methods and model systems, and a direct involvement of quantitative theoretical modeling.

On the theoretical side, the use of thin film equations, based on the lubrication approximation to the hydrodynamic equations for Newtonian liquids has been particularly successful [3]. As a consequence of this success, however, the inherent limitations of the classical lubrication approach to polymeric film have become evident as well. In the range where the polymer chain length begins to become comparable with the film thickness, the entanglement of the polymers in the film begins to influence the thin film dynamics, in particular at film rupture [4]. An example for such a signature is the profile of a decaying film in the vicinity of a hole opening in the film. This profile can, depending on polymer chain length and film thickness, be oscillatory or monotonely decaying. These effects have been related to the viscoelastic dynamics of the polymer films, and if this is correct, require an extension of the existing lubrication models to include these properties of the liquid.

In order to describe this and other non-Newtonian effects in thin films, various models have been discussed in the literature. They can roughly be grouped into three different classes (but mixtures of these appear as well). In the first, non-Newtonian behaviour is accounted for by assuming a nontrivial frequency dependence of the stress-strain relation in the form

$$\boldsymbol{\tau}(\omega) = \eta(\omega)\dot{\boldsymbol{\gamma}}(\omega) \tag{1}$$

where η is the shear viscosity of the liquid [5, 6]. In the second class, more general linear relationships between $\boldsymbol{\tau}$ and $\dot{\boldsymbol{\gamma}}$ are assumed; a typical example is the model put forward by Herminghaus et al. [19] which will be referred to in the paper [7, 8, 10]. These models can be extended to also account for so-called convective nonlinearities [9]. Nonlinearities become important when the shear in the film becomes large such that the stress tensor gets advected by the flow and rotated by the vorticity. The key case for which we want to apply the thin film equation is the decay of a capillary ridge. This experimentally well studied case does not involve large flow in the region in which we use the thin film equation. The same is true for the early dewetting dynamics of spinodal dewetting, for which our thin film equation can be applied as well. Therefore, we here restrict ourselves to linear relationships only.

In the third class, special assumptions are made on a nonlinear relationship between $\boldsymbol{\tau}$ and $\dot{\boldsymbol{\gamma}}$. This is e.g. the case for the power law fluids in which

$$\boldsymbol{\tau} = K\dot{\boldsymbol{\gamma}}^n \tag{2}$$

is assumed, with n often determined from fits to experimental data. This class comprises the case of shear-thinning and shear-thickening fluids, and since it allows a simple generalization of the thin film equations for Newtonian fluids, it has been frequently considered in the discussion of thin film phenomena [11, 12, 13, 14, 15].

All of these modelling approaches are often used in conjunction with additional ad hoc or phenomenological modelling assumptions. This has lead to conflicting interpretations of experimental results. As the models are fairly complex, often nonlinear, and do contain a number of different parameters which are often also unknown, the value of the conclusions drawn from these approaches remains hard to judge.

Given the success of the lubrication approximation for the dynamics of thin films of Newtonian character, we were prompted to look at this issue for the case of non-Newtonian liquids from a more general conceptual point of view. Here, we are not immediately concerned with the explanation of experimental results, but we rather pose the question of the derivation of a thin-film equation based on the lubrication approximation for the hydrodynamics of viscoelastic fluids.

The plan of this paper is thus as follows. We first define the class of viscoelastic model liquids which we will use throughout the paper and put it in the context of the phenomenological models recently discussed in the literature (Section 2). We then introduce some elementary concepts needed for the derivation of a thin film lubrication equation, which we subsequently obtain from a scaling analysis of the equations of viscoelastic hydrodynamics (Section 3). In Section 4, we study the shape of a liquid rim in a dewetting film, and conclude in Section 5 with a discussion of our finding in the context of recent results in the literature.

2 Viscoelastic hydrodynamics

2.1 Conservation laws

We here first state the hydrodynamic equations of viscoelastic media, and begin with the conservation laws. For the situations we will address, the liquid can be assumed to be incompressible with mass density ρ. The equation of mass conservation thus reduces to

$$\nabla \cdot \mathbf{u} = 0, \tag{3}$$

with the velocity field $\mathbf{u} = (u_x, u_y, u_z)$. The equation of momentum conservation is given by

$$\rho \frac{\mathrm{d}\mathbf{u}}{\mathrm{d}t} = -\nabla p_R + \nabla \cdot \boldsymbol{\tau}, \tag{4}$$

with the reduced pressure $p_R = p + V$. In this expression, p is the hydrostatic pressure, while the pressure induced by forces such as gravity or van der Waals type dispersion forces is given by V. The deviatoric (traceless) part of the stress tensor is $\boldsymbol{\tau}$ (which is symmetric). With $d/dt = \partial_t + \mathbf{u} \cdot \nabla$ we denote the material (or total) derivative, and with $\nabla = (\partial_x, \partial_y, \partial_z)$ the gradient operator.

2.2 Constitutive equations

In a Newtonian liquid $\boldsymbol{\tau}$ is proportional to the strain rate $\dot{\boldsymbol{\gamma}}$, i.e. to the gradient of the velocity field $\dot{\gamma}_{ij} = \partial_i u_j + \partial_j u_i$ (which holds for incompressible fluids). In a purely (linearly) elastic medium the stress would be proportional to the strain and not the strain rate. In order to describe a viscoelastic fluid one therefore needs a model constitutive relation for the dependence $\boldsymbol{\tau}(\dot{\boldsymbol{\gamma}})$ which interpolates between purely viscous and purely elastic behavior.

A frequently used example for such a viscoelastic model is the linear Jeffreys model (see [16, 17, 18])

$$\boldsymbol{\tau} + \lambda_1 \, \partial_t \boldsymbol{\tau} = \eta \left(\dot{\boldsymbol{\gamma}} + \lambda_2 \, \partial_t \dot{\boldsymbol{\gamma}} \right), \tag{5}$$

which contains two relaxation time constants λ_1 and λ_2 as well as the shear viscosity η. This model is sufficiently rich as it allows a purely viscous response of the liquid: sudden deformations allow for arbitrarily high stresses in the liquid. We note that it is equivalent to a special case of the generalized Maxwell model

$$\boldsymbol{\tau} = \boldsymbol{\tau}_1 + \boldsymbol{\tau}_2 \tag{6}$$

$$\boldsymbol{\tau}_\ell + \beta_\ell \, \partial_t \boldsymbol{\tau}_\ell = \mu_\ell \, \dot{\boldsymbol{\gamma}}, \quad \ell = 1, 2 \tag{7}$$

with a relaxation time constant $\beta_1 = \lambda_1$ and $\beta_2 = 0$ and the two shear viscosities μ_1, μ_2. The relationship between the generalized Maxwell and the Jeffreys model follows from the differentiation of $\boldsymbol{\tau}_2 = \mu_2 \dot{\boldsymbol{\gamma}}$ with respect to time; this yields the relationship between the parameters

$$\lambda_1 = \beta_1 \,, \ \eta = \mu_1 + \mu_2 \,, \ \lambda_2 = \lambda_1 \frac{\mu_2}{\mu_1 + \mu_2} \,. \tag{8}$$

Since the latter fraction obviously is always less than or equal to one, we generally have $\lambda_1 \geq \lambda_2$.

We note that in particular the model introduced by Herminghaus et al [7, 19] is equivalent to our model. The authors assume, like us, a stress tensor of the form of eq.(6) where $\boldsymbol{\tau}_1 = \mu_1 \dot{\boldsymbol{\gamma}}$, while $\boldsymbol{\tau}_2 = E\mathbf{S}$. Here E is the elasticity module and S_{ij} a tensor obeying the equation

$$(\partial_t + \omega_0) S_{ij} = \partial_i u_j + \partial_j u_i \,. \tag{9}$$

Identifying the relaxation frequency ω_0 with λ_2^{-1} and defining $\mu_2 = E\lambda_2$ then establishes the relationship between the models.

3 Lubrication approximation

We now turn to the derivation of a lubrication equation for the viscoelastic dynamics of the linear Jeffreys model, and begin by stating some general relationships we will use for this purpose in the following.

3.1 Parametrizing the thin film

For a flat liquid film on top of a solid substrate (we choose the coordinate system such that the xy-plane is the substrate surface) we can parameterize the surface of the liquid by a local film thickness $z = h(x, y, t)$. For incompressible liquids the time derivative of $h(x, y, t)$ is coupled to the flow field according to

$$\partial_t h = -\boldsymbol{\nabla}_{||} \cdot \int_0^h \mathbf{u}_{||} \, dz, \tag{10}$$

with the index $||$ denoting the xy-components of a vector parallel to the substrate; for example $\boldsymbol{\nabla}_{||} = (\partial_x, \partial_y)$ and $\mathbf{u}_{||} = (u_x, u_y)$.

At the free film surface the components of the stress tensor tangential to the surface vanish because we neglect the vapor phase (we consider a film effectively in vacuum). The normal component of the stress tensor is given by the Laplace pressure

$$(\boldsymbol{\tau} - p\,\mathbf{1}) \cdot \mathbf{n} = 2\,\sigma\,\kappa\,\mathbf{n}, \tag{11}$$

with the surface tension σ and the local normal vector pointing out of the fluid

$$\mathbf{n} = \frac{1}{\sqrt{1 + (\boldsymbol{\nabla}_{||} h)^2}} \left(-\boldsymbol{\nabla}_{||} h, 1 \right). \tag{12}$$

In eq.(11) we denote by $\mathbf{1}$ the 3×3 unit matrix; κ is the local mean curvature with the sign chosen such that the curvature of a spherical droplet of liquid is negative.

We further define the two tangential vectors $\mathbf{t}$ and $\mathbf{p}$ for later use such that all three vectors are mutually orthogonal and $\mathbf{t}$ points towards the up-hill direction

$$\mathbf{t} = \frac{1}{\sqrt{(\boldsymbol{\nabla}_{||}h)^2\left[1+(\boldsymbol{\nabla}_{||}h)^2\right]}}\left(\begin{array}{c}\boldsymbol{\nabla}_{||}h\\(\boldsymbol{\nabla}_{||}h)^2\end{array}\right) \tag{13}$$

$$\mathbf{p} = \frac{1}{\sqrt{(\boldsymbol{\nabla}_{||}h)^2}}\left(\begin{array}{c}-\partial_y h\\\partial_x h\\0\end{array}\right). \tag{14}$$

Finally, the substrate is supposed impermeable and we assume a Navier slip boundary condition for the velocity components parallel to the substrate

$$u_z = 0 \quad \text{and} \quad u_i = \frac{b}{\eta}\,\tau_{iz}, \tag{15}$$

with $i = x, y$ and the slip length b.

3.2 Scaling

For very thin films the length scale of the film thickness H is much smaller than the lateral length scale L parallel to the substrate surface. Thus $\varepsilon = H/L \ll 1$ is a natural small parameter which we will used to simplify the system presented in Sec. 2.

In order to retain the incompressibility condition (3) in every order in ε, the velocity scale normal to the substrate is ε times the velocity scale in the substrate plane U. The time scale is then given by $T = L/U$. We balance pressure, viscous forces and surface tension so that the pressure scale is

$$\frac{\eta}{T\,\varepsilon^2} = \frac{U\,\eta}{H\,\varepsilon} \tag{16}$$

and the scale for the surface tension is $U\,\eta/\varepsilon^3$.

The scaling of the strain rate tensor components $\dot{\gamma}_{ij}$ are determined by the scalings of velocity and length. If in addition corresponding components of the stress and strain rate tensor are on the same order (a scaling also used in [20] in the lubrication region) we get the following scaling relationships

$$\vec{r}_{||} = L\,\vec{r}^{\,*}_{||} \qquad (z, h, b) = H\,(z^*, h^*, b^*) \tag{17}$$

$$\vec{u}_{||} = U\vec{u}^{\,*}_{||} \qquad (t, \lambda_1, \lambda_2) = T\,(t^*, \lambda_1^*, \lambda_2^*) \tag{18}$$

$$u_z = \varepsilon\,U\,u_z^* \qquad (p, V, p_R) = \frac{\eta}{T\,\varepsilon^2}\,(p^*, V^*, p_R^*) \tag{19}$$

$$\sigma = \frac{U\,\eta}{\varepsilon^3} \tag{20}$$

$$\left(\begin{array}{ccc}\tau_{xx} & \tau_{xy} & \tau_{xz}\\\tau_{yx} & \tau_{yy} & \tau_{yz}\\\tau_{zx} & \tau_{zy} & \tau_{zz}\end{array}\right) = \frac{\eta}{T}\left(\begin{array}{ccc}\tau^*_{xx} & \tau^*_{xy} & \frac{\tau^*_{xz}}{\varepsilon}\\\tau^*_{yx} & \tau^*_{yy} & \frac{\tau^*_{yz}}{\varepsilon}\\\frac{\tau^*_{zx}}{\varepsilon} & \frac{\tau^*_{zy}}{\varepsilon} & \tau^*_{zz}\end{array}\right), \tag{21}$$

with the superscript "*" denoting the dimensionless quantities. The scaling of the stress tensor components τ_{ij} is, although physically motivated, not the only one used in the literature. In [21, 22], the in-plane components τ_{ij} with $i, j \in \{x, y\}$ are scaled as $\tau_{ij} = (\eta/\varepsilon^2\,\tau)\,\tau_{ij}^*$. For the nonlinear model used in [21, 22] this prescription is necessary in order to get a well-defined thin film limit. In the following, in order to avoid clumsy notation we drop the "*"; if not stated otherwise, all quantities from now on are to be considered dimensionless.

3.3 Dimensionless equations

The dimensionless form of the mass conservation (3) is

$$\boldsymbol{\nabla}\cdot\mathbf{u} = 0. \tag{22}$$

For the component of the momentum equation (4) parallel to the substrate we have

$$\varepsilon^2\,\mathrm{Re}\,\frac{\mathrm{d}u_i}{\mathrm{d}t} = \varepsilon^2\,\left(\partial_x\,\tau_{xi} + \partial_y\,\tau_{yi}\right) + \partial_z\,\tau_{zi} - \partial_i\,p_R, \tag{23}$$

with $i = x, y$ and for the normal component

$$\varepsilon^4\,\mathrm{Re}\,\frac{\mathrm{d}u_z}{\mathrm{d}t} = \varepsilon^2\,\left(\partial_x\,\tau_{xz} + \partial_y\,\tau_{yz} + \partial_z\,\tau_{zz}\right) - \partial_z\,p_R. \tag{24}$$

Here $\mathrm{Re} = \rho\,U\,L/\eta$ is the Reynolds number which we assume to be of order unity or smaller. In dimensionless form the linear Jeffreys model (5) is given by $(i = x, y, z)$

$$\begin{aligned} \tau_{ii} + \lambda_1\,\partial_t\tau_{ii} &= 2\,\left(\partial_i u_i + \lambda_2\,\partial_t\partial_i u_i\right) & (25)\\ \tau_{xy} + \lambda_1\,\partial_t\tau_{xy} &= \dot{\gamma}_{xy} + \lambda_2\,\partial_t\dot{\gamma}_{xy} & (26)\end{aligned}$$

$$\begin{aligned} \tau_{xz} + \lambda_1\,\partial_t\tau_{xz} &= \partial_z u_x + \lambda_2\,\partial_t\partial_z u_x + \left(\partial_x u_z + \lambda_2\,\partial_t\partial_x u_z\right)\,\varepsilon^2 & (27)\\ \tau_{yz} + \lambda_1\,\partial_t\tau_{yz} &= \partial_z u_y + \lambda_2\,\partial_t\partial_z u_y + \left(\partial_y u_z + \lambda_2\,\partial_t\partial_y u_z\right)\,\varepsilon^2 & (28)\end{aligned}$$

with $\dot{\gamma}_{xy} = \partial_x u_y + \partial_y u_x$. The other occurrences of components of $\dot{\boldsymbol{\gamma}}$ have been expanded in derivatives of $\vec{u}$.

The kinetic condition at the film surface (10) is invariant under rescaling, while the boundary condition at the substrate (15) becomes

$$u_z = 0 \quad \text{and} \quad u_i = b\,\tau_{iz}, \tag{29}$$

for $i = x, y$.

For the boundary condition at the film surface (11) we distinguish between the normal component

$$\begin{aligned} &\frac{\tau_{zz} - 2\left(\tau_{xz}\,\partial_x h + \tau_{yz}\,\partial_y h\right)}{1 + \varepsilon^2\,(\boldsymbol{\nabla}_{||}h)^2} + \varepsilon^2\,\frac{\left[\tau_{xx}\,(\partial_x h)^2 + \tau_{yy}\,(\partial_y h)^2 + 2\tau_{xy}\,\partial_x h\,\partial_y h\right]}{1 + \varepsilon^2\,(\boldsymbol{\nabla}_{||}h)^2} - \frac{p_R}{\varepsilon^2}\\ &\qquad = \frac{\sigma}{\varepsilon^2}\,\frac{\boldsymbol{\nabla}_{||}^2 h + \varepsilon^2\,\left[\partial_x^2 h\,(\partial_y h)^2 - 2\,\partial_x h\,\partial_y h\,\partial_x\partial_y h + \partial_y^2 h\,(\partial_x h)^2\right]}{\left[1 + \varepsilon^2\,(\boldsymbol{\nabla}_{||}h)^2\right]^{\frac{3}{2}}} \end{aligned} \tag{30}$$

and the two tangential components. Multiplying (11) with $\mathbf{t}$ and $\mathbf{p}$ from the left, we get

$$0 = \left[1 - \varepsilon^2 \left(\boldsymbol{\nabla}_{||} h\right)^2\right] \left(\partial_x h \, \tau_{xz} + \partial_y h \, \tau_{yz}\right) + \varepsilon^2 \left[\tau_{zz} \left(\boldsymbol{\nabla}_{||} h\right)^2 - \tau_{xx} \left(\partial_x h\right)^2 - \tau_{yy} \left(\partial_y h\right)^2 - 2 \, \tau_{xy} \, \partial_x h \, \partial_y h\right] \quad (31)$$

and

$$0 = \tau_{yz} \, \partial_x h - \tau_{xz} \, \partial_y h + \varepsilon^2 \left\{\left[(\partial_y h)^2 - (\partial_x h)^2\right] \tau_{xy} + (\tau_{xx} - \tau_{yy}) \, \partial_x h \, \partial_y h\right\} \quad (32)$$

respectively.

3.4 The thin film equation

We now pass to the lubrication equation which can be obtained as the lowest order equation in h. For the parallel and normal momentum equation (23) and (24) we have

$$\partial_z \tau_{zi} = \partial_i p_R \quad (33)$$

$$0 = \partial_z p_R, \quad (34)$$

respectively, with $i = x, y$. The constitutive equations (25) to (26) do not contain ε's. The leading order terms in (27) and (28) are

$$\tau_{xz} + \lambda_1 \, \partial_t \tau_{xz} = \partial_z u_x + \lambda_2 \, \partial_t \partial_z u_x \quad (35a)$$

$$\tau_{yz} + \lambda_1 \, \partial_t \tau_{yz} = \partial_z u_y + \lambda_2 \, \partial_t \partial_z u_y. \quad (35b)$$

The boundary conditions at the film surface $z = h(x, y, t)$ (30) to (32) are to leading order

$$p_R = - \boldsymbol{\nabla}_{||}^2 h + V(h), \quad (36)$$

$$0 = \partial_x h \, \tau_{xz} + \partial_y h \, \tau_{yz} \quad (37)$$

$$0 = \partial_x h \, \tau_{yz} - \partial_y h \, \tau_{xz}, \quad (38)$$

respectively. For $\boldsymbol{\nabla}_{||} h \neq \vec{0}$ the last two conditions can be summarized to

$$0 = \tau_{xz} = \tau_{yz}. \quad (39)$$

At this point it is useful to note the following: the flow field $\vec{u}$, the pressure p and therefore also the film shape h do only depend on τ_{xz} and τ_{yz}. Neither the constitutive equations for these fields (35a) and (35b) nor the boundary conditions (39) couple to the other stress components. We thus have a closed system of equations for $\vec{u}$, p, h, τ_{xz}, and τ_{yz} only.

To proceed further, we first note that according to the normal component of the momentum equation (34), p_R is independent of z. Integrating the parallel components of the momentum equation (33) with respect to z from z to $h(x, y, t)$ then yields

$$\tau_{iz} = (z - h) \, \partial_i p_R. \quad (40)$$

Upon substitution of (40) into the linear constitutive relation (35) we obtain

$$(1+\lambda_2\,\partial_t)\,\partial_z u_i \;=(1+\lambda_1\,\partial_t)\,[(z-h)\,\partial_i p_R]\,. \tag{41}$$

If we integrate this expression from 0 to z, use the boundary condition (29) for u_i and the value of τ_{iz} at $z=0$ from (41) we obtain

$$(1+\lambda_2\,\partial_t)\,(u_i+b\,h\,\partial_i p_R)=(1+\lambda_1\,\partial_t)\left[\left(\frac{z^2}{2}-hz\right)\,\partial_i p_R\right]. \tag{42}$$

Integrating this one more time from $z=0$ to $z=h(x,y,t)$ we find

$$\begin{aligned}(1+\lambda_2\,\partial_t)\left(\int_0^h u_i\,dz+b\,h^2\,\partial_i p_R\right)-\lambda_2\,\partial_t h\,\left(u_{i|_{z=h}}+b\,h\,\partial_i p_R\right)&\\ =-\,(1+\lambda_1\partial_t)\left(\frac{h^3}{3}\partial_i p_R\right)+\lambda_1\,\frac{h^2}{2}\,\partial_t h\,\partial_i p_R.&\end{aligned} \tag{43}$$

Using the kinematic condition (10) in (43) we obtain as the lubrication approximation to the linear Jeffreys model the equation

$$\begin{aligned}&\partial_t h+\lambda_2\left[\partial_t^2 h+\boldsymbol{\nabla}_{||}\cdot\left(\mathbf{u}_{||_{|z=h}}\partial_t h\right)\right]\\ &=\boldsymbol{\nabla}_{||}\cdot\left\{\left[(1+\lambda_1\,\partial_t)\,\frac{h^3}{3}+(1+\lambda_2\,\partial_t)\,b\,h^2\right]\boldsymbol{\nabla}_{||}\,p_R\right\}\\ &\quad-\boldsymbol{\nabla}_{||}\cdot\left[\left(\frac{h^2}{2}\,\lambda_1+b\,h\,\lambda_2\right)\,\partial_t h\,\boldsymbol{\nabla}_{||}p_R\right]\end{aligned} \tag{44}$$

with p_R at the film surface given by (36).

We are now left to find an expression for $\mathbf{u}_{|_{z=h}}$ in terms of $h(x,y,t)$. Observing that (42) can be written as an ordinary differential equation in time

$$u_i+\lambda_2\partial_t u_i=g_i \tag{45}$$

where

$$g_i \;:=\; -(1+\lambda_2\partial_t)\,bh\partial_i p_R+(1+\lambda_1\partial_t)\left[\left(\frac{z^2}{2}-hz\right)\,\partial_i p_R\right], \tag{46}$$

we can represent the solution as

$$u_i=\frac{1}{\lambda_2}\int_{-\infty}^{t}\mathrm{e}^{-\frac{t-t'}{\lambda_2}}\,g_i(x,y,z,t')\,dt' =: \frac{1}{\lambda_2}\mathcal{L}[g_i]. \tag{47}$$

Integration by parts can be used to simplify (47) at $z=h(x,y,t)$ to the form

$$\lambda_2\vec{u}_{||_{|z=h}}=-\left(\lambda_1\frac{h^2}{2}+\lambda_2 bh\right)\boldsymbol{\nabla}_{||}p_R+(\lambda_2-\lambda_1)\left(\frac{h^2}{2}\mathbf{Q}_{||}-h\mathbf{P}_{||}\right), \tag{48}$$

where

$$\mathbf{Q}_{||} = \frac{1}{\lambda_2}\mathcal{L}\left[\boldsymbol{\nabla}_{||}p_R\right], \quad \mathbf{R}_{||} = \frac{1}{\lambda_2}\mathcal{L}\left[h\boldsymbol{\nabla}_{||}p_R\right], \tag{49}$$

or equivalently

$$\mathbf{Q}_{||} + \lambda_2\partial_t\mathbf{Q}_{||} = \boldsymbol{\nabla}_{||}p_R, \quad \mathbf{R}_{||} + \lambda_2\partial_t\mathbf{R}_{||} = h\boldsymbol{\nabla}_{||}p_R. \tag{50}$$

Using this in (44) we find the lubrication equation

$$\begin{aligned}(1+\lambda_2\partial_t)\partial_t h + (\lambda_2-\lambda_1)\boldsymbol{\nabla}_{||}\cdot\left[\left(\frac{h^2}{2}\mathbf{Q}_{||} - h\mathbf{R}_{||}\right)\partial_t h\right] \\ = \boldsymbol{\nabla}_{||}\cdot\left\{\left[(1+\lambda_1\,\partial_t)\,\frac{h^3}{3} + (1+\lambda_2\,\partial_t)\,b\,h^2\right]\boldsymbol{\nabla}_{||}\,p_R\right\}\end{aligned} \tag{51}$$

The system of eqs. (50) and (51) is the central result of the paper. It constitutes a lubrication equation for the linear Jeffreys (generalized Maxwell) model without any further assumptions on the flow of the viscoelastic medium on the surface.

It is worth to note some general features of this novel lubrication model. Firstly, the dependence of the Jeffreys model on higher order derivatives of the stress and strain rate tensors is reflected by a second derivative of the film height. Secondly, even for this simple model system the equations are more involved due to the presence of nonlinear terms with mixed time and space derivatives.

We finally comment on the limiting cases the equation assumes in specific limits. For $\lambda_2 \to 0$ it collapses to a single equation. This limit corresponds to the simplest Maxwell model with only one stress tensor contribution. In the case $\lambda_1 = \lambda_2$ we recover the thin film equation of Newtonian liquid, multiplied on both sides by a factor $(1+\lambda_1\,\partial_t)$.

4 The shape of a rim in a dewetting film

As an application of the novel lubrication equation we investigate the issue of the shape of the rim of a dewetting viscoelastic thin film. In ref.[19], Herminghaus et al. have shown that in viscoelastic thin films based on the generalized Maxwell model, both oscillatory rim profiles as well as monotonely decaying profiles are possible, in accord with experiment.

In order to address this question we consider the linear stability of the system (50) and (51). For this it is enough to consider the 2D situation of a cross-section of the rim. Since we are not interested in the behaviour near the contact-line, we further neglect Van der Waals forces represented by $V(h)$.

Technically, we perform an analysis on the same level as in [19]. We only look at the linear problem of the decay of the capillary response the opening hole creates towards the flat film state. For this we shift the coordinate system to the frame co-moving with the rim, i.e. we let

$$h(x,t) = h(\xi,t), \quad Q(x,t) = Q(\xi,t), \quad R(x,t) = R(\xi,t), \tag{52}$$

with $\xi = x - s(t)$ and where Q is the first component of $\mathbf{Q}_{||}$ and R is the first component of $\mathbf{R}_{||}$ in 2D. This yields

$$\begin{aligned}
&\partial_t h - \dot{s}\partial_\xi h + \lambda_2\left(\partial_t^2 h - 2\dot{s}\partial_t\partial_\xi h + \dot{s}^2\partial_\xi^2 h - \ddot{s}\partial_\xi h\right)\\
&\quad + (\lambda_2 - \lambda_1)\partial_\xi\left[(\partial_t h - \dot{s}\partial_\xi h)\left(\frac{h^2}{2}Q - hR\right)\right]\\
&= \partial_\xi\left[-\left(\frac{h^3}{3} + bh^2\right)\partial_\xi^3 h - \partial_t\left\{\left(\lambda_1\frac{h^3}{3} + \lambda_2 bh^2\right)\partial_\xi^3 h\right\}\right.\\
&\quad \left. + \dot{s}\partial_\xi\left\{\left(\lambda_1\frac{h^3}{3} + \lambda_2 bh^2\right)\partial_\xi^3 h\right\}\right],
\end{aligned} \tag{53}$$

together with

$$Q + \lambda_2\partial_t Q - \lambda_2\dot{s}\partial_\xi Q = -\partial_\xi^3 h \tag{54}$$

and

$$R + \lambda_2\partial_t R - \lambda_2\dot{s}\partial_\xi R = -h\partial_\xi^3 h \tag{55}$$

If we then perturb around a flat reference state with $h_0 = const.$, $Q = 0$ and $R = 0$, by setting

$$h = h_0 + \delta\cdot\varphi, \quad Q = \delta\cdot\psi_1, \quad R = \delta\cdot\psi_2 \tag{56}$$

and by assuming a quasi-steady state in which the shape of the rim changes only slowly and the speed $\dot{s}$ is constant, we find for the perturbation equations for (53), (54), (55), keeping only the $O(\delta)$ terms

$$-\dot{s}\partial_\xi\varphi + \lambda_2\dot{s}^2\partial_\xi^2\varphi + \left(\frac{h_0^3}{3} + bh_0^2\right)\partial_\xi^4\varphi - \dot{s}\left(\lambda_1\frac{h_0^3}{3} + \lambda_2 bh_0^2\right)\partial_\xi^5\varphi = 0 \tag{57}$$

and

$$\psi_1 - \lambda_2\dot{s}\partial_\xi\psi_1 = -\partial_\xi^3\varphi, \quad \psi_2 - \lambda_2\dot{s}\partial_\xi\psi_2 = -h_0\partial_\xi^3\varphi. \tag{58}$$

Note that equation (57) does not contain any contributions from ψ_1 or ψ_2 and hence we can simply solve it by making the normal mode *ansatz* $\varphi = \mathrm{e}^{\omega\xi}$, requiring that the solutions decay to $\varphi \to 0$, since $h \to h_0$, $Q = 0$ and $R = 0$ as $\xi \to \infty$. Hence, the solutions must always have ω with a *negative real part.*

However, we find that in the equation for the growth rate

$$-\dot{s} + \lambda_2\dot{s}^2\omega + \left(\frac{h_0^3}{3} + bh_0^2\right)\omega^3 - \dot{s}\left(\lambda_1\frac{h_0^3}{3} + \lambda_2 bh_0^2\right)\omega^4 = 0 \tag{59}$$

all coefficients $\dot{s}\left(\lambda_1\frac{h_0^3}{3} + \lambda_2 bh_0^2\right)$, $\left(\frac{h_0^3}{3} + bh_0^2\right)$, $\lambda_2\dot{s}^2$ and $\dot{s}$ are positive constants. From the form of the polynomial we can thus conclude that normal modes with negative real ω will never be a solution of equation (59). Consequently, the solutions which decay to zero as $\xi \to \infty$ have to be oscillatory, as in the special case of the Newtonian fluid with $\lambda_1 = \lambda_2$. This is in contrast to the results by [19], where it is argued that viscoelasticity will introduce a change in shape to a monotone decaying rim towards the undisturbed portion of the film.

5 Conclusions

In this paper, we have derived a novel thin film equation for viscoelastic media based on a linear Jeffreys model. As a first application of this equation we have studied the rim profile in a dewetting thin film, and find that it always has oscillatory behaviour. This result is in contrast to the finding by Herminghaus et al.[19] which is based on the same viscoelastic model of the liquid, but which is then subjected to additonal assumptions.

We believe that this apparent discrepancy can be related to the treatment of slip. In refs.[23], [24] two of us (A.M. and B.W.), together with others, have studied the properties of a lubrication model which can be derived when the slip-length is larger than the thickness of the undisturbed film. This model, which is based on a Newtonian dynamics of the liquid, exhibits a transition from solutions with oscillatory decay of the profile to those with a monotone decay.

Therefore we are led to conclude that the essential mechanism underlying the morphology change in the rim profiles is not due to the bulk properties of the liquid (be they Newtonian or not), but rather determined by its hydrodyamic interaction with the underlying substrate. However, in order to fully understand the dynamic behaviour of rupturing thin films, the model derived here needs to be extended to account for convective nonlinearities, which may indeed become relevant near the contact line [**?**].

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