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Non-linear dynamics and self-similarity in the rupture of ultra-thin viscoelastic liquid coatings

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The influence of viscoelasticity on the dewetting of thin liquid films is revealed by means of theory and numerical simulations in the inertialess limit. Three viscoelastic models are employed to analyze the dynamics of the film, namely the Oldroyd-B, Giesekus, and FENE-P models. We revisit the linear stability analysis (LSA) first derived by [Román et al., Eur. Phys. J. E., 20, 185-200, 2000] for a Jeffreys film to conclude that all three models formally share the same dispersion relation. For times close to the breakup singularity, the self-similar regime recently discovered by [Moreno-Boza et al., Phys. Rev. Fluids, 5, 034600, 2020], where the dimensionless minimum film thickness scales with the dimensionless time until breakup as \( t \propto -0.665 \epsilon^{-1/3} \), is asymptotically established independently of the rheological model. The spatial structure of the flow is characterized by a Newtonian core and a thin viscoelastic boundary layer at the free surface, where polymeric stresses become singular as \( \epsilon \to 0 \). The Deborah number and the solenoidal-elongational inertia both affect the breakup time but for the high aspect the linear/dewetting pattern and asymptotic flow structure close to \( \epsilon \to 0 \), which is shown to be the result of three-dimensional simulations and is so called that bulk viscoelasticity was done to study the experimental observations of dewetting of polymeric liquids near the glass transition.

1 Introduction

Thin liquid films can be found in a sheer number of technological applications, nature, and everyday phenomena. For instance, they play important roles in geological flows, medicine, or mammalian physiology, where biofluids are present, as it is the case of surfactant-laden films covering the alveoli of the lung in mammals physiology, where biofluids are present, or in polymeric solutions close to the glass transition. There are a few studies dealing with the development of the nascent vdW-triggered instability in ultra-thin films.

In particular, their analysis for zero inertial effects shows that in the limit of a polymeric melt, the growth rate experiences a singularity controlled by a critical Weissenberg number (the product of Capillary and Deborah numbers), upon which it blows up over a narrow band of wavelengths. This non-physical singularity reminds of a solid-like infinitely fast response to forcing, and is shown to be only overcome by including finite inertia of the liquid. In addition, electro-hydrodynamical effects are considered in the earlier work, which also encountered the aforementioned singularity.

By way of contrast, the lubrication approximation of the equations of motion incorporating viscoelastic models has been extensively used. Alternatively, one aspect of the viscoelastic dewetting flow that has received considerable attention is the retraction dynamics of the liquid rims formed during the late stages of the film evolution.

In particular, for zero inertial effects that show the breakup of polymeric melt, the growth rate experiences a singularity controlled by a critical Weissenberg number (the product of Capillary and Deborah numbers), upon which it blows up over a narrow band of wavelengths. This non-physical singularity reminds of a solid-like infinitely fast response to forcing, and is shown to be only overcome by including finite inertia of the liquid. In addition, electro-hydrodynamical effects are considered in the earlier work, which also encountered the aforementioned singularity.

By way of contrast, the lubrication approximation of the equations of motion incorporating viscoelastic models has been extensively used. Alternatively, one aspect of the viscoelastic dewetting flow that has received considerable attention is the retraction dynamics of the liquid rims formed during the late stages of the film evolution. However, the spatial structure of the thinning flow during the first stages of the spinodal dewetting process prior to the formation of the precursor film and liquid rim structures, most notably the associated rupture times and characteristic wavelengths, the possible existence of self-similar regimes appearing near the rupture singularity, and the performance of three-dimensional simulations, are all of them aspects that have been studied as extensively as far as we know. Furthermore, the dewetting patterns observed in refs. 21,36,38 of polymeric films heated close to the glass transition are not yet fully understood. Here, we aim to address some of these questions by studying, for the first time, the linear stability derived from the complete Stokes

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The paper is organised as follows. In §2 we present the mathematical models used to describe the dewetting flow of a viscoelastic ultra-thin films. In §3 we provide a linear stability analysis of the complete Stokes equations coupled with the disperse rheological models, and then we perform an comprehensive study comparing the latter results with previous ones obtained with the lubrication approximation. In §4 we carry out two-dimensional numerical simulations of the viscoelastic Stokes equations to unravel the asymptotic self-similar regimes during film thinning for different Deborah numbers and solvent-to-total viscosity ratios. We then focus on the viscoelastic self-similar problem in §5 to explain the observations made in §4. In §5 we provide three-dimensional direct numerical simulations of the complete viscoelastic Stokes equations to compare the dewetting patterns both with experiments and with their Newtonian counterpart. Concluding remarks are finally presented in §6.

2 Mathematical description

We consider the incompressible flow of a non-Newtonian thin liquid film initially resting on a solid substrate and immersed in a passive fluid ambient. It is well known that, in the non-wetting case, the van der Waals (vdW) intermolecular interactions between the film and the substrate induce the instability of the flat film solution when its initial height $h_0$ is below approximately 100 nm. Indeed, the vdW forces exceed the stabilizing surface tension force for perturbations of sufficiently large wavelength, finally leading to film rupture. Let $\gamma$ denote the constant surfactant face tension coefficient, $\mu_s$ the solvent viscosity, and $\mu_p$ the polymeric contribution to the viscosity, such that $\mu_t = \mu_s + \mu_p$ is the total effective viscosity and $\beta = \mu_p/\mu_t$ the solvent-to-total viscosity ratio. Note that $0 \leq \beta \leq 1$, where the limits $\beta \to 0$ and $\beta \to 1$ correspond to the cases of a polymer melt and a Newtonian film, respectively. By selecting

$$\lambda = \frac{h_0}{\nu_s}, \quad l_c = \frac{A}{6\pi \mu_s \lambda}, \quad l_s = \frac{6\pi \mu_s \lambda}{A}, \quad \rho_v = \rho_s = \rho = \frac{A}{6\pi \lambda^3},$$

(1)

as the relevant scales of length, velocity, time, pressure, stresses, and intermolecular potential, respectively, where $A$ is the Hamaker constant, the dimensionless augmented Stokes equations of motion read

$$\nabla \cdot \mathbf{u} = 0, \quad \mathbf{u} - \nabla (\gamma \mathbf{I} : \mathbf{T} - \mathbf{n}) = \mathbf{0}, \quad \chi \in \mathcal{Y},$$

(2)

where $\mathcal{Y}$ is the fluid domain, $\mathbf{u}$ is the velocity field, $\gamma = k^{-1}$ is the intermolecular potential derived for the particular case of the vdW force between two parallel surfaces, $\mathbf{T} = -\mathbf{\nabla} \cdot \mathbf{P}$ is the stress tensor of the fluid, $\mathbf{P} = 1/2 (\mathbf{\nabla} \mathbf{u} + (\mathbf{\nabla} \mathbf{u})^T)$ is the rate-of-strain tensor, and $\mathbf{n}$ is the symmetric polymer stress tensor.

Historically, many constitutive equations have been used to determine the polymeric stress tensor (see refs. 43–46 for exhaustive reviews). One of the simplest and most commonly used models for dilute polymer solutions is the Oldroyd-B fluid, which can be derived from kinetic theory considering the polymer chains as non-interacting Hookean dumbbells. Here we only consider a single relaxation time of the chains, $\lambda$, in contrast with refs. 47–49, which introduced a discrete spectrum of relaxation times. However, as discussed by ref. 50, the assumption of a single relaxation time is a reasonable simplification, since the chains with the largest relaxation time eventually dominate the rate of stretching. The relaxation time $\lambda$ immediately defines a Deborah number, $De = \lambda / \tau = \lambda c (6\pi \mu_s \lambda)$, as the ratio between $\lambda$ and the relevant characteristic time scale $\tau$, defined in eqn. (1). On selecting the scales (1), the dimensionless evolution equation for $\mathbf{n}$ following the Oldroyd-B model reads

$$De \dot{\mathbf{n}} - \mathbf{n} = 2(1 - \beta) \mathbf{E}, \quad \chi \in \mathcal{Y},$$

(3)

where $\mathbf{v} = \mathbf{\nabla} \mathbf{u} + (\mathbf{\nabla} \mathbf{u})^T - \mathbf{n}$ is the upper-convected Maxwell model. Linearisation of the upper-convected Maxwell and Oldroyd-B models yields the Maxwell's 72 and Jeffrey's 53 viscoelastic models, respectively. In contrast, the limit $\beta \to 1$ leads to the Stokes equations for a New-
A viscoelastic film covering a flat substrate, and the finite extensibility of the polymer chains might affect the dewetting dynamics. More realistic models, that take into account such finite extensibility effects, are the FENE-P model, which stands for \textit{finitely-extensible-nonlinear-elastic} and \textit{P} for the Peterlin’s closure idea, and the Giesekus model, first derived in ref. \textsuperscript{37}. The polymeric constitutive equation in the FENE-P frame of work reads

$$\mathbf{D} \mathbf{E} = \left[ \frac{1}{1 - \beta^2} + \frac{De}{1 - \beta^2} \right] \mathbf{E} \mathbf{E} - \frac{2(1 - \beta)}{1 - 3 \beta^2} \mathbf{E} \mathbf{e} \mathbf{e} \mathbf{E} \mathbf{e} + \beta \mathbf{e} \mathbf{E} \mathbf{e}$$

where the dimensionless parameter $\beta$, usually known as the extensibility parameter, denotes the ratio between the maximum extension length and the equilibrium length of the dumbbells, which is $R_0$. A function of the spring constant, the Boltzmann constant and the temperature. In the infinitely extensible limit, $\beta \rightarrow \infty$, the Oldroyd-B model (3) is recovered. Finally, the third model considered in the present work is the Giesekus model, whose constitutive equation reads

$$\mathbf{D} \mathbf{E} = \frac{De}{1 - \beta} \left( \mathbf{E} \mathbf{e} \mathbf{E} - \frac{2(1 - \beta)}{1 - 3 \beta^2} \mathbf{E} \mathbf{e} \mathbf{E} \mathbf{e} \right) + \beta \mathbf{e} \mathbf{E} \mathbf{e}$$

where $\alpha$ is a dimensionless parameter that accounts for the anisotropy of the drag coefficient of the polymer chains within the fluid. In the limit $\alpha \rightarrow 0$, it reduces to the Oldroyd-B model (3).

At the free surface, $x \in \partial \mathcal{F}$, we impose the kinematic condition, which precludes interfacial mass transfer, and the surface stress balance,

$$\mathbf{u} \cdot (\beta \lambda \mathbf{e} - \mathbf{u}) = 0$$

and

$$\mathbf{T} \cdot \mathbf{n} = \mathbf{n} \cdot \mathbf{u} + \mathbf{n} \cdot \mathbf{u} = 0$$

respectively, where $\mathbf{C} = A/(6\pi \eta \lambda)$ is the Capillary number, which can be expressed in terms of the molecular length, $a = |A/(6\pi \eta \lambda)|^{1/2}$, and $\lambda(= \lambda(\omega/\omega_0))^{-1}$. Here $x$ is the parametrisation of the free surface, and $\mathbf{n}$ its unit normal vector. At the solid substrate, the no-slip and no-penetration boundary conditions, $\mathbf{u} = 0$, are fulfilled.

\section{Linear stability analysis}

To analyze the effect of viscoelasticity on the initial growth of perturbations, we perform a linear stability analysis of the \textit{wdW}-\textit{unstable} viscoelastic film considering, for the first time, the complete equations of the different rheological models. The results will then be compared with those obtained from the lubrication theory developed in refs. \textsuperscript{30,32}.

\subsection{Stokes equations}

The dispersion relation is derived by introducing the normal-mode decomposition

$$\mathbf{u} = \mathbf{u} \mathbf{u} + \beta \lambda \mathbf{e} \mathbf{e} + O(\epsilon^2)$$

into eqns (2), (6a), (6b), and either (3), (4), or (5), and retaining terms up to $O(e)$, where $\epsilon < 1$ is the relative amplitude of the perturbation, $a$ is the growth rate, which should be understood as a real quantity, and $k$ is the wavenumber. The dispersion relation is therefore given by

$$\left(1 + De \right) \cosh(2k) - 3 \left[ \sinh(2k) - 2k \right] = 0$$

which yields the same dispersion relation as (8), but perhaps due to errors or typos in their derivation these authors obtained a dispersion relation with missing terms.

It is important to emphasise that the Giesekus model yields exactly the same dispersion relation, since the term proportional to $\alpha$ is non-linear and the base-flow velocity is zero. In the case of the FENE-P constitutive equation, the functional form of the dispersion relation is also the same, but the Deborah number has to be redefined as $De \rightarrow De(1 - 3/2\beta)$. Notice also that in the limits $De \rightarrow 0$ or $\beta \rightarrow 1$, eqn (8) yields the growth rate corresponding to a Newtonian film, namely $a = (3 - Ca^{-1})/( \sinh(2k) - 2k)/(2k(1 + 2Ca + \cosh(2k)))$, deduced for instance in refs. \textsuperscript{27,39}.

Figure 2 shows the amplification curves $a(k)$ obtained from eqn (27), for $\beta = (0.0, 0.1, 0.5, 0.9)$ in panels 2(a-d), respectively, for different values of $De$ indicated in the legends. The filled circles are the growth rates extracted from the two-dimensional numerical simulations by imposing the corresponding wavenumber and streamwise periodicity conditions (more details are provided in §4), displaying excellent agreement. The most remarkable feature of fig. 2 is the fact that the most amplified wavenumber, $k_m$, is independent of the rheological parameters and depends only on $Ca$, which can be readily explained by noticing that the viscoelastic parameters $\beta$ and $De$ only appear in the coefficients of $\omega_a$ and $\omega_0$ in eqn (8), as already noted in \textsuperscript{26,34} in their analyses. Indeed, one can find an implicit equation for $k_m$ upon maximizing the solution given in Appendix A, eqn (27), with respect to $k$. This in fact yields a product of two separate functions of $k_m$, one of which only vanishes for $k_m = 0$. The non-trivial factor yields the transcendental equation

$$0 = 6Ca_k \left[ 4k_m^2 + 1 + 2k_m^2 \right] + 2k_m \left[ Ca \left(4k_m^2 + 3\right) + k_m^2 \left(1 - 2k_m^2\right) \right] \cosh(2k_m)$$

which indeed shows that $k_m$ depends exclusively on $Ca$, as suggested by the results of Figs. 2(a-d). Consequently, the characteristic length of the dewetting patterns should not be affected by the viscoelasticity of the film. Although eqn (9) has no closed-form solution for $k_m$, a small-$Ca$ expansion provides

$$k_m = \sqrt{\frac{Ca}{30}} \left(1 - \frac{27}{80}Ca + 3.677Ca^2 + 0.053Ca^3 + 0.0001Ca^4 \right)$$

for \textit{wdW}-\textit{unstable} film described by the linear Jeffrey's model, which should yield the same dispersion relation as (8), but perhaps due to errors or typos in their derivation these authors obtained a dispersion relation with missing terms.
The double-starred symbols indicate the results extracted from the two-dimensional numerical simulations of Stokes equations (22a) coupled with the Oldroyd-B model (23). Panel (c) and (d) shows the maximum growth rate, $\omega_m$, obtained numerically from the exact dispersion relation (8) and Maxwell’s models, when taking $\beta=0.1$ (solid lines), $\beta=0.9$, and $\beta=3.16$ (dashed lines), respectively.

Fig. 2 Analytical results $(a)$ for $Gr = 0.1$ (curves 1, 2, and 3) and $(b)$ $\beta = 0.1$, $(c)$ $\beta = 0.5$, and $(d)$ $\beta = 0.9$, and different values of $De$ indicated in the legends. The symbols indicate the results extracted from the two-dimensional numerical simulations of Stokes equations (22a) coupled with the Oldroyd-B model (23). Panel (c) and (d) show the maximum growth rate $\omega_m$, obtained numerically from the exact dispersion relation (8) (solid lines), and the analytical results (10) obtained from the lubrication approximation (dashed lines), taking $Ca = 0.01$ ($\tanh(wa) = 10$) and $Ca = 0.1$ ($\tanh(wa) = 3.16$) in $(c)$ and $(d)$, respectively.

From the expression above we can infer that the rupture time $t_{eq}$ and, in consequence, the maximum growth rate $\omega_{eq}$, are slightly affected by the viscoelastic effects if the capillary number $Ca$ is small or, in other words, if the initial film height is much larger than the molecular length scale, $h_0/\alpha \gg 1$, as clearly observed in Figs. 2(e) and (f). Indeed, eqn (12) reveals that $De$ and $\beta$ appear in terms which are $O(Ca)$ and higher in the $Ca$-expansion.

It proves useful to provide the expression of the rupture time scaled with the characteristic time $t_c = \mu_0/\gamma$, which makes use of the molecular length scale $\alpha$ instead of the initial film thickness $h_0$. In particular, we note here that the use of $\alpha$ as substitution for $h_0$ in the characteristic scales is useful to analyse the non-linear dynamics of the flow near rupture, studied in §4. Expressing $t_c$ rescaled with $\omega$, as a function of $h_0/\alpha$ instead of $Gr$ yields (27,28,60),

$$
t_c = \frac{4}{3} \left( \frac{h_0}{\alpha} \right)^3 + \frac{18}{5} \left( \frac{h_0}{\alpha} \right)^5 - \frac{3}{700} \frac{h_0}{\alpha} \left( 2899 + 140(\beta - 1)De [27 + 5De(5\beta - 3)] + O(Ca^3) \right) - 3 \left( -4\omega_0^2 + \frac{1}{4} \right) \tanh^2(2\omega_0^2).
$$

(13)

It is also interesting to note that the dispersion relation (8) is exactly the same as the one obtained from linear viscoelastic models, namely the Jeffreys’s and Maxwell’s models, when taking the limit of a polymer melt, $\beta \rightarrow 0$, and arbitrary $De$, which reads

$$
\omega = \sqrt{(3 - 6\alpha^2)/(4Ca^2) \tanh(2\omega_0^2) - 2}.
$$

(14)

Note that the maximum growth rate $\omega_m$ becomes singular in this limit when $De \approx De^* = 4/(3Ca^2) - 18/5 = 1.797Ca/700$ as provided.
by substituting $k = k_0 \approx \sqrt{3(27 C_a/40)}$ in eqn (14). The appearance of such critical value of $De$ and the subsequent singularity in the temporal growth rate has been previously discussed in\textsuperscript{28,29,34}, where a solid-like behaviour is accompanied by an almost instantaneous response to an applied forcing. Liquid inertia is seen to be a regularization mechanism, as demonstrated in\textsuperscript{38}.

Fig. 2(a) shows the temporally unstable branch for increasing values of $De$, where a peak at $k = k_0$ is seen to develop as $De \to De^\ast$. In figs. 2(a) and (b) this singularity is displayed for the maximum growth rate $\omega_m$, which diverges as $(De - De^\ast)^{-1}$ for $\beta = 0$. In this limiting case, the dynamics is completely dictated by the polymer melt, which behaves as a viscoelastic solid. Nevertheless, the limit of eqn (14) when $\omega \to 0$, since the polymer chains never relax due to the fact that $\lambda > \epsilon$.

In the limit $De \to \infty$ and arbitrary $\beta$, the dispersion relation (8) reduces to $\omega = \sqrt{(2C_\nu^{-1} - 3)(2C_\nu \sinh(2\nu))}$, which diverges as $\beta \to 1$. Here, since $\lambda > \epsilon$, the polymer chains neither relax nor do they contribute to the viscosity of the suspension (see eqn 3). Hence, the appropriate time scale only involves the viscosity of the solvent $\mu_s$, and the growth rate should be rescaled as $\omega \to \beta \omega$, which yields a parameter-free amplification curve with the same functional form as that of a Newtonian film.

### 3.2 The lubrication approximation

Under the lubrication approximation of the Jeffrey's model, the equivalent expressions of eqns (8) and (15) were first obtained by Safran and Klein\textsuperscript{30}, and refined later on by Blossey et al.\textsuperscript{32} considering also wall slippage. Neglecting slippage, the dispersion relation obtained from the lubrication model reads

$$\omega = (1 + D \beta \omega)(1 - D \omega)(3 - C_\nu \lambda^2) \lambda^2 / 3 = 0.$$  \hspace{1cm} (16)

This lubrication dispersion relation can be also derived from eqn (8) by expanding in powers of $k$, resulting in an identical expression except for the order $O(k^4)$ term, $-9/5$. From eqn (16) we can take the limit $De \to \infty$,

$$\omega = \frac{k^2(1 - C_a \lambda^2)}{3\beta}$$ \hspace{1cm} (17)

to be compared with its Stokes counterpart (15). Note that, in ref.\textsuperscript{21}, our parameter $\beta$ is equivalent to the ratio between their $\lambda_1$ and $\lambda_1$ time scales, which are the relaxation times associated to the viscous rate-of-strain of the solvent and to the polymeric stress, respectively. In addition, the limit $\beta \to 0$ of a polymer melt, under the lubrication approximation, reads

$$\omega = \frac{k^2(1 - C_a \lambda^2)}{De^2(2C_\nu(\lambda^2 - 3) + 3)}$$ \hspace{1cm} (18)

to be compared with the corresponding Stokes result (14).

From the lubrication dispersion relations (16)–(18) we can obtain the most amplified wavenumber, which is independent of $De$ and $\beta$ as anticipated from the full Stokes equations in eqns (9),
Fig. 4 Minimum film thickness as a function of the rescaled time to rupture, $\tau/\beta$ for different values of the Deborah number, $De$, indicated in the legend, and $\beta = 0.1$ in (a,c,e), and $\beta = 0.5$ in (b,d,f), and the three different viscoelastic models, namely Oldroyd-B in (a,b), Giesekus in (c,d), and FENE-P in (e,f). The lower inset in (b) illustrates the consistent $1/3$, $1/5$, and $1/7$, behaviour of the polyelectrolyte stress $\sigma_{11}$, vertical velocity $v$, and transversal increments $\Delta y$, respectively, evaluated at $x = 0, y = h_{\text{min}}(t)$ for $De = 10$. 
The numerical method was adapted from the one employed in ref. [27], where the reader can find a detailed technical explanation. The scales used to study the near-rupture dynamics are the molecular scales [20], unless otherwise specified.

Fig. 4 shows the minimum thickness of the film, $h_{min} = h(s, 0)$, and the instantaneous exponent $n = d \log_{10} h_{min}/d \log_{10} (t/\beta)$ in the insets, as functions of the rescaled time to rupture, $\tau = (t_n - t)/\beta$. In particular, Figs. 4(a,b) show the results obtained from the Oldroyd-B model, Figs. 4(c,d) those from the Giesekus model, and Figs. 4(e,f) those from the FENE-P model. These figures evidence that, independently of the viscoelastic constitutive equation and for any value of $\beta$, $De$, $L^2$, and $\alpha$, the ultimate self-similar regime that is established as $\tau \to 0$ is that of a Newtonian liquid film, recently discovered in ref. [27], and where $h_{max} = 0.663 t^{1/3}$, where $t = \tau/\beta$ is the time to rupture non-dimensionalised with the viscosity of the Newtonian liquid. Hence, the fact that $\tau/\beta$ is the appropriate time that makes all the figures collapse close to rupture means that only the solvent plays a role close to the singularity. More importantly, to elucidate how the polymeric stresses affect the transient regime and the spatial structure of the flow as the singularity is approached, Fig. 5 shows the evolutions of two different viscoelastic films with $Ca = 0.01$ (or $h_o/a = 10$), where the colour plot shows the scalar quantity $\sigma : E$.

4.1 Numerical simulations

To elucidate the nonlinear and near-rupture dynamics of the viscoelastic thin film, we have performed numerical simulations of the complete Stokes equations (2), coupled with either the Oldroyd-B (3), Giesekus (5), or FENE-P (4) models for the polymeric stress tensor. Taking into account the fact that the local flow close to the rupture singularity loses memory of the initial conditions, it proves convenient to change the characteristic length scale to non-dimensionalise the mathematical model, substituting $h_o$ by $a$,

$$t \approx \frac{A}{h_o^2}$$

We consider first a planar two-dimensional film starting from rest and whose free surface is slightly perturbed by a harmonic disturbance at $t = 0$, namely

$$u(x, 0) = 0, \quad h(x, 0) = h_o/a(1 - \cos(\pi x)) \quad \text{with} \quad k < k_c,$$

for $0 \leq x \leq 1/k$, thus triggering the vDW-induced instability.

The numerical method was adapted from the one employed in ref. [27], where the reader can find a detailed technical explanation. The scales used to study the near-rupture dynamics are the molecular scales [20], unless otherwise specified.

Fig. 5 shows the minimum thickness of the film, $h_{min} = h(s, 0)$, and the instantaneous exponent $n = d \log_{10} h_{min}/d \log_{10} (t/\beta)$ in the insets, as functions of the rescaled time to rupture, $\tau = (t_n - t)/\beta$. In particular, Figs. 4(a,b) show the results obtained from the Oldroyd-B model, Figs. 4(c,d) those from the Giesekus model, and Figs. 4(e,f) those from the FENE-P model. These figures evidence that, independently of the viscoelastic constitutive equation and for any value of $\beta$, $De$, $L^2$, and $\alpha$, the ultimate self-similar regime that is established as $\tau \to 0$ is that of a Newtonian liquid film, recently discovered in ref. [27], and where $h_{max} = 0.663 t^{1/3}$, where $t = \tau/\beta$ is the time to rupture non-dimensionalised with the viscosity of the Newtonian liquid.
4.2 Near-rupture flow and viscoelastic boundary layer

The results of section 4.1 will now be explained by means of a careful analysis of the simulation results for \( \tau \ll 1 \). The projection of the momentum equation (2) in the \( x \) direction can be estimated at the scale of the film, \( \sim h_{\text{film}} \), to yield the balance

\[
\frac{\partial \xi}{\partial t} - \frac{\partial \psi}{\partial x} = \frac{\partial^2 \psi}{\partial x^2} - 1/3 \frac{\partial}{\partial x} \left( h_{\text{film}} \right)^{2/3},
\]

leading to the asymptotic rupture law \( h_{\text{film}} \sim t^{1/3} \) deduced in [27], and confirmed in the viscoelastic flow under study by the results of Fig. 4. The \( x \)-momentum equation can also be used to estimate the characteristic polymeric stresses, \( \sigma_i(\tau) \). Indeed, \( -\partial \psi - \partial \psi/\partial t = \sigma_i(\tau) = \phi_i \), where \( \phi_i \) is the characteristic van der Waals potential, leading to \( \sigma_i \sim \tau^{-1} \), in agreement with the inset of Fig. 4(b). The thickness and length of the viscoelastic boundary layer, respectively given by \( \delta(\tau) \) and \( \zeta(\tau) \) (see Figs. 8 and 9), were obtained from the evaluation of the spatial distribution of the polymeric stresses for decreasing values of \( \tau \). Figure 6(b) shows the distribution of the rescaled polymeric stress \( (\tau/\beta)\sigma_1 \) as a function of the rescaled transverse coordinate, \( (\tau/\beta)^{1/3} \xi \), and evaluated at the symmetry plane, \( \xi = 0 \).

4.3 The leading-order self-similar solution

In view of the results of Fig. 4, one may anticipate the appearance of a self-similar regime in which \( h_{\text{film}} \) follows the asymptotic thinning law first reported in our previous work [27], namely \( h_{\text{film}} \sim t^{1/3} \), whereas the maximum velocity should scale as \( u \sim t^{-2/3} \). Moreover, this law is expected to be achieved for arbitrary values of \( \alpha_0 \) and \( \beta > 1 \), according to the non-linear simulations. The self-similar exponents numerically obtained resemble those obtained in ref. [27], in which the Stokes equations exhibit a similarity solution of the first kind with a wedge-shaped free surface and an associated opening angle of \( 37^\circ \) off the solid substrate. In what follows, we shall demonstrate that viscoelastic film thinning is dictated by the same asymptotic law as that of a Newtonian liquid. The leading-order description of the fluid flow is the same as that given in ref. [27] whereas the viscoelastic stress tensor is seen to obey a homogeneous problem whose solution, at leading order in powers of \( \tau \), is the trivial one \( \sigma = 0 \) as \( \tau \rightarrow 0 \). Indeed, by letting \( x = (\tau/\beta)^{1/3} y = (\tau/\beta)^{1/3} \eta \), \( u = (\tau/\beta)^{-2/3} \mu \), \( v = (\tau/\beta)^{-2/3} \nu \), \( p = (\tau/\beta)^{-1} p \), \( h = (\tau/\beta)^{1/3} h \), and \( \epsilon_i = (\tau/\beta)^{-1} \epsilon_i \), with \( i \) (or \( j \)) = (1, 2), one finds the consistent leading-order elliptic system of partial differential equations

\[
\begin{align*}
U_{\xi} + V_{\eta} &= 0, \tag{22a} \\
U_{\xi\xi} + U_{\eta\eta} + \Sigma_{1,\xi} + \Sigma_{1,\eta} &= -R_{\xi} \frac{3h}{h^3}, \tag{22b} \\
V_{\xi\xi} + V_{\eta\eta} + \Sigma_{2,\xi} + \Sigma_{2,\eta} &= R_{\eta}, \tag{22c}
\end{align*}
\]
Fig. 8 Fractal time evolution showing the self-similar collapse of the film shapes of an Oldroyd-8 film with $\theta_0 = 10, \beta = 0.5, De = 10$. The colour plots and contours show the self-similar viscoelastic stress $\Sigma_{ij}$ ($\theta(t)$) which is centred to a boundary layer at the free surface as $\tau \to 0$, in the remaining components of the viscoelastic stress tensor.

stems from eqn (2), to be integrated in $-\infty < \xi < \infty$ and $0 < \eta < f(\xi)$, where $f(\xi)$ is to be obtained as part of the solution. Eqs. (22a)–(22c), need to be integrated with the boundary conditions (6), which in self-similar variables read

\begin{align*}
(1 + \xi^2) P - \xi^2 \left( \Sigma_{11} - 2\Sigma_{22} \right) - 2 \left( \Sigma_{22} + 2\Sigma_{66} \right) + \\
2 \xi \left( \Sigma_{12} + \Sigma_{66} + V \right) &= 0, \tag{23a} \\
\xi \left( \Sigma_{22} - \Sigma_{11} + 2 \left( \Sigma_{66} - V \right) \right) &= 0, \tag{23b} \\
\xi \left( \Sigma_{12} + \Sigma_{66} + V \right) &= 0, \tag{23c}
\end{align*}

along the free surface $\eta = f(\xi)$, $U = V = 0$ at the substrate wall, $\eta = 0$, and $\delta = 0$ at the symmetry axis $\xi = 0$. The remaining boundary conditions at the numerical infinity $\xi = \infty$ are handled as in ref.\textsuperscript{27}. Note that capillarity forces are subdominant, and the leading-order balance is established between viscous and vdW forces. In addition, it is important to emphasise that eqns (22a)–(23c) are independent of the viscoelastic model. For instance, the Oldroyd-8 model yields the system of equations

\begin{align*}
\left( \xi + 3M \right) \Sigma_{11} &= \left( \eta + 3V \right) \Sigma_{11} - \left( 3 - 6\xi \right) \Sigma_{11} + 6\Sigma_{12} = 0, \\
\left( \xi + 3M \right) \Sigma_{22} &= \left( \eta + 3V \right) \Sigma_{22} - \left( 3 - 6\xi \right) \Sigma_{22} + 6\Sigma_{22} = 0, \tag{24b} \\
\left( \xi + 3M \right) \Sigma_{12} &= \left( \eta + 3V \right) \Sigma_{12} - \left( 3 - 6\xi \right) \Sigma_{12} + 6\Sigma_{12} = 0, \tag{24c}
\end{align*}

at $O(\tau^{-2})$, which completes the self-similar description. The system formed by eqns (24a)–(24c) constitutes a homogeneous linear system for the components of the leading-order polymer stress tensor $\Sigma_{ij}$, independent of $De$ and $\beta$. Note that the trivial solution $\Sigma_{ij} = 0$ yields the solution given in ref.\textsuperscript{27} for the flow field, providing a free surface whose far-field shape is linear, i.e., $f(\xi) = \xi - \xi_0 \tan \theta_0$, for some $\xi_0$, compatible with eqn (23c) for $\xi > 1$ and vanishing velocities. The numerical solution of eqns (22a)–(24c) (see ref.\textsuperscript{27} for details on the numerical method) confirms that this angle is indeed $\theta_0 \sim 37^\circ$, with accompanying vanishing polymeric stresses. The self-similar collapse is illustrated in Fig. 7 for a Giesekus film with no precursor. The study of the rheological boundary layer sitting on the free surface $\eta = f(\xi)$ appearing at the following order would constitute a formidable mathematical task, intrinsic to each viscoelastic model, and not to be pursued in this paper.

5 Three-dimensional numerical simulations

The experimental patterns shown in refs.\textsuperscript{21,36,38} are thus far unexplained. To elucidate if these patterns arising in polymeric films...
Fig. 9 Evolutions of a three-dimensional thin liquid film with $h_0/a = 5$, $\epsilon = 0.05$, and $h_{\text{prec}} = 0.35$ in (a-e), and $\epsilon = 0.1$, $h_{\text{prec}} = 0.3$ in (f), for aqueous solutions. The Newtonian liquid film is shown in (a-e), and the non-Newtonian films are shown in the remaining panels with the corresponding viscoelastic dimensionless numbers being (f-j) $\beta = 0.1$ and $De = 10$, (k-o) $\beta = 0.1$ and $De = 1$, and (p-t) $\beta = 10^{-5}$ and $De = 100$. The labels indicating time are scaled with $(1)$.
where the zero velocity, initial condition, we impose a randomly corrugated surface and less thickness of the precursor film. As for the three-dimensional potential such that the intermolecular potential may be replaced by

\[ \phi = h^{-3} - h_{\text{prec}}^{-1} \]  

(see for instance ref. 26) in eqns (2), where \( h_{\text{prec}} \) is the dimensionless thickness of the precursor film. As for the three-dimensional initial condition, we impose a randomly corrugated surface and zero velocity.

\[ h(\mathbf{x}, 0) = 1 + \sum_{l=0}^{N} \sum_{j \in \mathcal{N}_l} A_j \cos \left( \mathbf{k}_j \cdot \mathbf{x} + \phi(j) \right) \]

\[ \mathbf{a}(\mathbf{x}, 0) = 0 \]  

(26)

where \( \mathbf{x} \) is the in-plane position vector, \( A_j = \epsilon(i^l / \sqrt{p}) \)

\[ \beta \gamma \gamma^2 / \nu(i, j) \]  

being a Gaussian distribution, \( \nu \) the spectral exponent, \( \mathbf{k}_j = 2\pi / \lambda(l, j) \), with \( \lambda(l, j) \) the size of the computational domain in the \( x \) and \( y \) directions, and \( \lambda(l, j) \) the unit vector in the \( x \) direction.

Fig. 9 shows snapshots of the time evolution of a three-dimensional Newtonian thin liquid film in the upper row, and the corresponding non-Newtonian film modeled with the Oldroyd-B constitutive equation in the bottom row. In particular, in both simulations the initial height of the film is \( h_{0}/a = 5 \)

\[ \text{the Newtonian case. However, the dewetting pattern is qualitatively similar in both scenarios, thus the morphology shown by the Oldroyd-B, Giesekus, and FENE-P models, we have shed light on some aspects of their linear and near-rupture dynamics. In particular, analytical estimations of the rupture times and associated wavelengths of the dewetting patterns are given by means of linear theory in terms of the relevant dimensionless governing parameters. In particular, it is found that such wavelength is independent from the values of the solvent-to-total viscosity ratio and Deborah numbers, therefore being an exclusive function of the Capillary number regardless the rheological model employed. Additionally, by means of two-dimensional numerical simulations of the Stokes equations coupled with non-linear viscoelastic models, we have shown that for times close to the singularity, the Newtonian self-similar regime obtained in our previous work is always achieved. This phenomenon occurs independently of the rheological behaviour of the planar film, the consequence being that the viscoelastic stresses remain confined in a boundary layer placed at the free surface, and whose thickness becomes smaller as breakup is approached. Moreover, we have also performed three-dimensional numerical simulations of a planar viscoelastic film with random initial conditions, to determine if the dewetting patterns are substantially different from their Newtonian counterpart. However, the final morphologies found in both cases are close to the rim, as anticipated by Fig. 5. Therefore, other effects must be taken into account to explain such patterns, namely the residual stresses, the slippage of the film which can be large in glassy films or the viscoelastic nature of the material. Aside from the patterns observed by ref. 27, the advanced post-processing techniques used by ref. 26 could be potentially used here to infer and characterize the viscoelastic properties of the film from the 3D patterns, namely the relaxation time of the polymer chains or the nonlinear material parameters introduced in the Giesekus and FENE-P models. However, this task is out of the scope of the present work.

6 Conclusions and future prospects

Despite the relevance of ultra-thin viscoelastic and glassy coatings, some fundamental questions about their dynamics have remained overlooked. By considering three viscoelastic models, i.e., the Oldroyd-B, Giesekus, and FENE-P models, we have shed light on some aspects of their linear and near-rupture dynamics. In particular, analytical estimations of the rupture times and associated wavelengths of the dewetting patterns are given by means of linear theory in terms of the relevant dimensionless governing parameters. In particular, it is found that such wavelength is independent from the values of the solvent-to-total viscosity ratio and Deborah numbers, therefore being an exclusive function of the Capillary number regardless the rheological model employed. Additionally, by means of two-dimensional numerical simulations of the Stokes equations coupled with non-linear viscoelastic models, we have shown that for times close to the singularity, the Newtonian self-similar regime obtained in our previous work is always achieved. This phenomenon occurs independently of the rheological behaviour of the planar film, the consequence being that the viscoelastic stresses remain confined in a boundary layer placed at the free surface, and whose thickness becomes smaller as breakup is approached. Moreover, we have also performed three-dimensional numerical simulations of a planar viscoelastic film with random initial conditions, to determine if the dewetting patterns are substantially different from their Newtonian counterpart. However, the final morphologies found in both cases are
qualitatively similar, which means that the viscoelastic rheology is not the cause of the dewetting patterns reported in refs. 23,36,38. Here we suggest that such morphologies might be a consequence of the residual and thermal stresses, a manifestation of viscoplastic behaviour, or a strong slippage of these rheologically complex films. Although these effects are out of the scope of the present work, their study constitutes an exciting direction for future contributions.

A The analytical expression for the growth rate

The closed-form solution to the dispersion relation (8) for the growth rate is available as follows:

\[
\alpha = \frac{1}{4\beta Ca De (1 + 2k^2 + \cosh(2\kappa))} \left\{ 8\beta Ca De \left( 3Ca - k^2 \right) \times \right. \\
\left. \sinh(2\kappa) - 2\kappa \left[ 1 + 2k^2 + \cosh(2\kappa) \right] + 2\kappa \left( 3CaDe + 2Ca k^2 + Ca - De k^2 \right) + \right. \\
\left. De \left( k^2 - 3Ca \right) \sinh(2\kappa) + 2CaDe \cosh(2\kappa) \right\}^{1/2} \\
- 6Ca De k + 3Ca De \sinh(2\kappa) - 4Ca k^3 - \\
2Ca (1 + \cosh(2\kappa)) + 2De k^3 - 2De \cosh(2\kappa). \right)
\]

which is provided here for the first time (to the best of our knowledge). The second root of (8) is always negative for all \( k \). Note that in refs. 24,29 only the dispersion relation (8) is given.

Conflicts of interest

There are no conflicts to declare.

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Notes and references
