Dynamic Instability of Thin Viscoelastic Films under Lateral Stress

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We study the influence of lateral stress on the stability of thin viscoelastic films. The free surface of a deposited film under stress is shown to undergo an instability initiated by an anisotropic diffusion of the polymer molecules. This instability ultimately results in the formation of holes provided that the initial surface fluctuations are larger than a critical value. The latter is found to decrease when increasing the stress. An increase of the holes number density with the stress is therefore predicted. Most interestingly, the holes number density is also predicted to increase when increasing the molecular weight of the polymers. Additionally, we demonstrate that the friction of the substrate suppresses any spatial coherence between holes on large length scales. These predictions explain recent experimental observations made on thin spin-coated polystyrene films [G. Reiter *et al.*, Nat. Mater. **4**, 754 (2005)].

Thin polymer films occur widely in industrial processes, and play a major role in the current manufacturing of nanodevices. Consequently, they have been the subject of a large amount of recent work [1–4]. A major issue is their stability, the lack of which leads to the rather common observation of appearing holes. However, the physical mechanism (spinodal dewetting, heterogeneous nucleation, …) leading to the formation of these holes is still a matter a debate [5,6]. Some time ago Safran and Klein [7] predicted that stability could be provided using high molecular weight polymer films. Nevertheless, such films have been shown then to dewet rather rapidly [8,9]. Moreover, the number density of appearing holes happens to increase with the molecular weight, up to 3000 kg · mol^{-1} [10].

It has been theoretically predicted [11], and experimentally shown [12], that the most broadly used fabrication process of thin polymeric films, i.e., the spin coating process, leads to the presence of residual stresses in the films. The residual stresses relaxes over a long time τ_r that increases with the molecular weight of the polymers. Therefore, all the films which are not annealed above the glass transition temperature (T_g) for a long enough time ($t \gg \tau_r$) must be under stress. The initial state of polymer films has been recently shown to have a direct influence on their subsequent stability [9]. Reiter *et al.* noticed that the density of holes forming above T_g in polystyrene (PS) films conserved below the glass transition decreases when increasing the conservation time. Eventually, very old films happened to be stable. These features have been attributed to the presence of residual stresses slowly relaxing (over years) below T_g. How precisely these residual stresses may lead to film rupture was, however, not discussed by these authors.

The purpose of this Letter is to show how residual stresses can indeed be responsible for the formation of holes in highly viscoelastic films, independently of the role played by the disjoining pressure, explaining the ob-

servations of Reiter *et al.* [8,9]. We also show how the interactions between the film and the substrate suppress long range order in the spatial distribution of holes, in good agreement with the observations of Jacobs *et al.* [13].

Let us first focus on a Hookean elastic film, of modulus G deposited on a slippery flat substrate. Hereafter, we will neglect the possible influence of the disjoining pressure. We will also restrict our concern to a two-dimensional linear analysis in the xOz plane (see Fig. 1). We assume that the film originally displays small thickness variations around the mean value h_i, characterized by a wavelength $\lambda = 2\pi/k$. A mean horizontal normal stress σ_0, either tensile ($\sigma_0 > 0$) or compressive ($\sigma_0 < 0$), is then applied to the film, leading to the thickness:

$$h(x) = h_0[1 + \epsilon \cos(kx)], \tag{1}$$

where h_0 is related to the initial mean thickness h_i and the mean stress σ_0 by the relation $h_0 = h_i \exp(-\sigma_0/G)$. The stress will then present small spatial variations of the same wavelength:

$$\sigma_x(x) = \sigma_0[1 + \delta \cos(kx)] \tag{2}$$

with ϵ and $\delta \ll 1$. The undulated surface displays with the
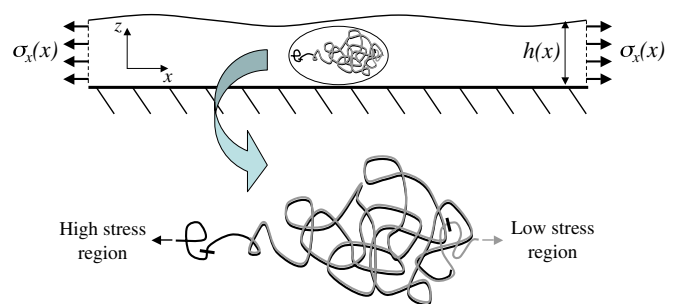

FIG. 1 (color online). Schematic representation of a polymer chain diffusing in an inhomogeneously stressed melt. The limits of the initial conformation are marked by the small strokes.

horizontal axis a small angle $\theta \simeq \epsilon$ to first order. In these conditions, the stresses σ_x and σ_z, in the horizontal and vertical directions, respectively, do not depend on the vertical coordinate z at first order in ϵ, but the shear stress σ_{xz} does. The momentum equation along the Ox axis integrated over the thickness of the film imposes the relation:

$$\partial_x(h\sigma_x) + \gamma \partial_{xx} h \partial_x h = 0, \tag{3}$$

where γ is the surface tension of the film. From this first relation we deduce that $\delta = -\epsilon$. The mechanical equilibrium at the surface of the film imposes that the stress matches the Laplace pressure:

$$\sigma_z + \sigma_x(\partial_x h)^2 - 2\sigma_{xz}\partial_x h = \gamma \partial_{xx} h. \tag{4}$$

This second relation gives $\sigma_z(x) = -\gamma h_0 k^2 \epsilon \cos(kx)$, at first order in ϵ. Then, from σ_x and σ_z, we deduce $\sigma_{xz}(x, z) = [z/2(1 + \nu)](\gamma h_0 k^2 - \nu \sigma_0) k \epsilon \sin(kx)$, where ν is the Poisson ratio. The resulting elastic energy surface density is $E_{el} = h(\sigma_x e_x + \sigma_z e_z + 2\sigma_{xz} e_{xz})/2$, where $e_x = (\sigma_x - \nu \sigma_z)/G$, $e_z = (\sigma_z - \nu \sigma_x)/G$, and $e_{xz} = 2(1 + \nu)\sigma_{xz}/G$ are the normal strains in the two directions and the shear strain, respectively [14]. One can show that the contribution of the shear is negligible when $(h_0 k)^2 \ll 3(1 + \nu)/2\nu^2 \sim 1$. The difference in elastic energy (per unit surface) between an undulated film and a flat film under the same horizontal stress is then given by

$$\delta E_{el}(x) = -\frac{1}{2} h_0 \frac{\sigma_0^2}{E}\left[\left(1 - \frac{2\nu \gamma h_0 k^2}{\sigma_0}\right)\epsilon \cos(kx)\right.$$
$$\left. + \left[1 - \left(\frac{\gamma h_0 k^2}{\sigma_0}\right)^2\right][\epsilon \cos(kx)]^2\right] \tag{5}$$

at second order in ϵ. In addition, the interfacial energy $E_{surf} = \gamma\sqrt{1 + (\partial_x h)^2}$ is enhanced by the surface undulations:

$$\delta E_{surf}(x) = \frac{1}{2}\gamma h_0^2 k^2 \epsilon^2 [\sin(kx)]^2. \tag{6}$$

We can now write the surface average of the total energy variation $\delta E = \delta E_{el} + \delta E_{surf}$ at lower order:

$$\langle \delta E \rangle = -\frac{h_0}{4}\left(\frac{\sigma_0^2}{G} - \frac{(\gamma h_0 k^2)^2}{G} - \gamma h_0 k^2\right)\epsilon^2. \tag{7}$$

This quantity is negative for wave numbers smaller than

$$k_0 = \frac{|\sigma_0|}{\sqrt{\gamma h_0 G}} \tag{8}$$

at first order in σ_0/G, if $|\sigma_0|$ is smaller than G. The corresponding minimum wavelength is $\lambda_0 = 2\pi\sqrt{\gamma h_0 G}/|\sigma_0|$. We can verify that the condition $h_0 k_0 \ll 1$ may be achieved. Indeed, for film thicknesses smaller than 200 nm as in [8,9,13], and using the typical values $G \simeq 10^5$ Pa, and $\gamma \simeq 20$ mN/m, the quantity $\gamma/h_0 G$ is larger than 1. Hence, the latter inequality reads $|\sigma_0|/G \ll \gamma/h_0 G$, which is easily achieved. We will restrict the following study to cases where $|\sigma_0| \ll G$, and to the first order in σ_0/G, since it allows us to neglect σ_z and σ_{xz}, and

also to stay in the frame of application of linear elasticity. Note, however, that the physical mechanisms described in this study have no reasons to be significantly modified if $\sigma_0/G > 1$.

The fact that the energy of an undulated film is smaller than the one of a flat film implies that if a film under stress has any way to relax, it will relax towards an undulated shape. Hence, purely elastic stressed films are not unstable, but viscoelastic films should be. This is the same idea as for the Asaro, Tiller, and Grinfeld (ATG) instability for solid metals [15]. Note that the possible role of an ATG process for thin polymer films has already been proposed in [16].

Polymer melts are known to be viscoelastic [17,18]. This property is due to the fact that each polymer chain can be viewed as confined in a tube by the entanglements it forms with the surrounding chains. These entanglements are responsible for the elastic properties, and the elastic modulus G is related to the number P of monomers between entanglements by the relation $G = kT/a^3 P$, where kT is the Boltzmann coefficient times the temperature, and a is the monomers size. A stressed melt displays a nonzero mean orientation of the tubes. However, the chains can diffuse parallel to their tube by "reptation," and the tube orientation order is lost when a chain reptates out of its tube and forms a new one. As a result, the elastic energy stored between the entanglements is dissipated by the time $\tau_r = R^2/D$ the chains diffuse over their size R, where D is their diffusion coefficient. One of the simplest linear viscoelasticity model is Maxwell's model [19], which relates the stress σ and its time derivative $\dot{\sigma}$ to the strain rate $\dot{e}$. For example, in the Ox direction ($\dot{e}_x = \partial_x v_x$, where v_x is the horizontal velocity), the constitutive rheologic equation reads

$$\sigma_x - \nu \sigma_z + \tau_r(\dot{\sigma}_x - \nu \dot{\sigma}_z) = \eta \dot{e}_x, \tag{9}$$

where $\eta = G\tau_r$ is the steady state viscosity of the melt. This model leads to an exponential decrease of the stress over the characteristic time τ_r at zero strain rate.

Let us now consider the case of a polymer chain diffusing in a nonhomogeneously stressed melt. The chain will then be more likely to reptate towards the less stressed direction, since it makes the mean tube orientation, and hence the chain elastic energy, to decrease faster (see Fig. 1). This anisotropic diffusion gives birth to a volume flux $J_x = -(D/kT)\partial_x \mu_{el}$, related to a local chemical potential μ_{el}, which is simply the elastic energy volume density times the volume $V = a^3 N$ of a chains.

If such an anisotropic diffusion takes place in a thin polymer film, the displacements of the particles in the film are associated to displacements of particles at the surface (due to volume conservation). The potential of a chain at any height z within the film is thus equal to the potential of a chain at the surface, which comprises an interfacial energy term $V\gamma \partial_{xx} h$. Therefore, the horizontal diffusive flux resulting from the inhomogeneities of the chemical potential in a film for which the thickness and the stress are

given by Eqs. (1) and (2) is

$$J_x(x) = \frac{DV}{kT}\left(\frac{\sigma_0^2}{G}\delta + \gamma h_0 k^2 \epsilon\right)k\sin(kx) \qquad (10)$$

at first order in ϵ and δ. Hereafter, all of our results will be given at first order in ϵ and δ.

Let us consider the case of a viscoelastic film interacting with the substrate through a friction force $f_r = \zeta v_x(z = 0)$ by surface unit, where ζ is the friction coefficient assumed to be constant, and $v_x(z = 0)$ is the slip velocity. The horizontal velocity v_x can be considered as independent of the z coordinate if the slippage length $b = \eta/\zeta$ is large compared to the thickness h_0 of the film [20]. Now, the theoretical prediction for b is $a(N^3/P^2)$ [21], which gives $b \sim 50\ \mu$m ($a = 0.5$ nm, $N = 1000$, and $P = 100$), and it can be even increased if the substrate is a liquid. From [9] the slippage length can be evaluated to be larger than $100\ \mu$m, while the studied films are thinner than 200 nm. Then, the momentum equation (3) integrated over the thickness of the film reads $\zeta v_x = \partial_x(h\sigma_x) + \gamma\partial_{xx}h\partial_x h$, leading to

$$\zeta v_x = -h_0\sigma_0(\epsilon + \delta)k\sin(kx). \qquad (11)$$

Completing the equations set (9)–(11), with the volume conservation equation

$$\partial_t h = -\partial_x[h(v_x + J_x)], \qquad (12)$$

one can build the two relations that give the time evolution of σ_x and h. At order zero, one obtains a decreasing mean stress $\sigma_0(t) = \sigma_0\exp(-t/\tau_r)$, and a constant mean thickness h_0. At first order, one obtains two coupled linear equations for ϵ and δ:

$$\dot{\epsilon} = -\left[\frac{DV}{kT}\gamma h_0 k^2 - \frac{h_0\sigma_0}{\zeta}\right]k^2\epsilon - \left[\frac{DV}{kT}\frac{\sigma_0^2}{G} - \frac{h_0\sigma_0}{\zeta}\right]k^2\delta$$

$$\dot{\delta} = -\left[\frac{Gh_0}{\zeta}\right]k^2\epsilon - \left[\frac{Gh_0}{\zeta} + \frac{1}{\tau_r k^2}\right]k^2\delta. \qquad (13)$$

One of the eigensolutions of this system always gives a decrease of ϵ and δ with time. The other one corresponds to $\delta \simeq -\epsilon$ for $k > 1/\Delta$, where $\Delta = \sqrt{h_0 b} \gg h_0$, and can give positive growth rates for ϵ (see Fig. 2). For $k > 1/\Delta$, the initial growth rate of the instability is given by the relation

$$\frac{\dot{\epsilon}}{\epsilon} = \frac{4}{\tau_0}\left(1 + \frac{\sigma_0}{G}\right)\left[\frac{k^2}{k_0^2}\left(1 - \frac{k^2}{k_0^2}\right) - \frac{1}{(k_0\Delta)^2}\right], \qquad (14)$$

where the growth rate $1/\tau_0$ is

$$\frac{1}{\tau_0} = \frac{1}{4}\frac{DV}{kT}\frac{\sigma_0^4}{\gamma h_0 G^2}. \qquad (15)$$

Notice that when σ_0 gets of the order of G, the distinction between tensile and compressive stress becomes relevant. The growth rate given by Eq. (14) is positive for wavelengths larger than $\lambda_0 = 2\pi/k_0 = 2\pi\sqrt{\gamma h_0 G}/|\sigma_0|$, in agreement with the preliminary energetic approach, and
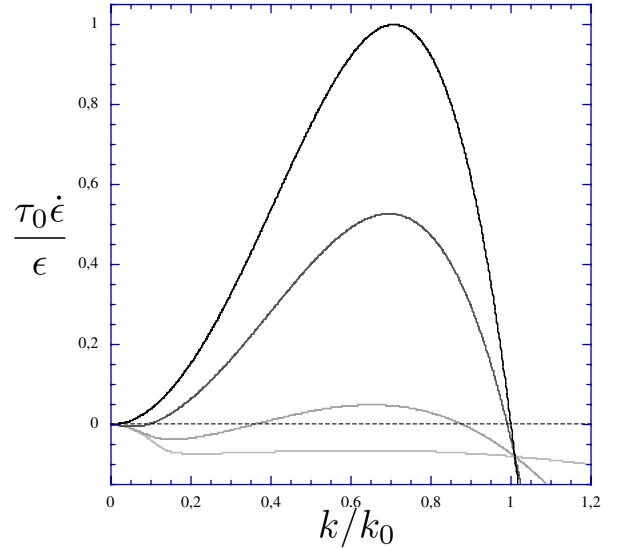

FIG. 2 (color online). Initial growth rate of the instability scaled with the maximum growth rate $1/\tau_0$ (with $\tau_r/\tau_0 = 10$), as a function of the wave number k scaled with k_0, for $(k_0\Delta)^2 = 1$ (light gray), 10, 100, and 1000 (black).

the maximum initial growth rate is reached for $k = k_0/\sqrt{2}$ ($\lambda = \sqrt{2}\lambda_0$). On the other hand, the growth rates are negative for shorter wavelengths due to surface tension, and also for wavelengths larger than Δ due to the friction on the substrate that screens off the elastic interactions [9,22,23]. The film is hence unstable when $\lambda_0 < \Delta$, which reads $|\sigma_0|/G > \sqrt{\gamma/bG}$. From the evaluation of b, and the typical values of γ and G proposed above, we deduce that $\sqrt{\gamma/bG} < 10^{-2}$. Then, a film can be destabilized with a stress as weak as $10^{-2}G$. Now, the time evolution of ϵ, for $k \gg 1/\Delta$, can be easily computed at lower order in σ_0/G:

$$\epsilon = \epsilon_0\exp\left\{\frac{4}{\tau_0}\frac{k^2}{k_0^2}\left[\tau_r(1 - e^{-t/\tau_r}) - \frac{k^2}{k_0^2}t\right]\right\}. \qquad (16)$$

Notice that the amplitude of the instability presents a maximum $\epsilon_{\max}(k)$ at time $t = 2\tau_r\ln(k_0/k)$, for the stress $\sigma_0(t)$ falls down to zero for times larger than τ_r (see Fig. 3). As a result, the maximum amplitude of the instability $\epsilon_{\max} \simeq \epsilon_0\exp(0.4\tau_r/\tau_0)$ does not correspond to the fastest mode $k_0/\sqrt{2}$, but to the slightly slower mode $k \simeq 0.53k_0$ [more precisely, $(k/k_0)^2[1 - 4\ln(k/k_0)] = 1$]. The existence of a maximum of the amplitude of this stress driven instability implies that the process can lead to the formation of holes only if $\tau_0 \ll \tau_r$, or more precisely if $\epsilon_{\max} \gtrsim 1$, which is achieved if

$$2\left[\frac{kT}{DV}\frac{\gamma h_0}{\tau_r G^2}\ln\left(\frac{1}{\epsilon_0}\right)\right]^{1/4} \lesssim \frac{|\sigma_0|}{G}. \qquad (17)$$

Since values of $|\sigma_0|/G$ are smaller than 1, the inequality (17) cannot be achieved for large values of the film thickness h_0. Indeed, $kT/\gamma a^2$ is generally of order unity, and the bulk diffusion coefficient of an N-monomers chain in an
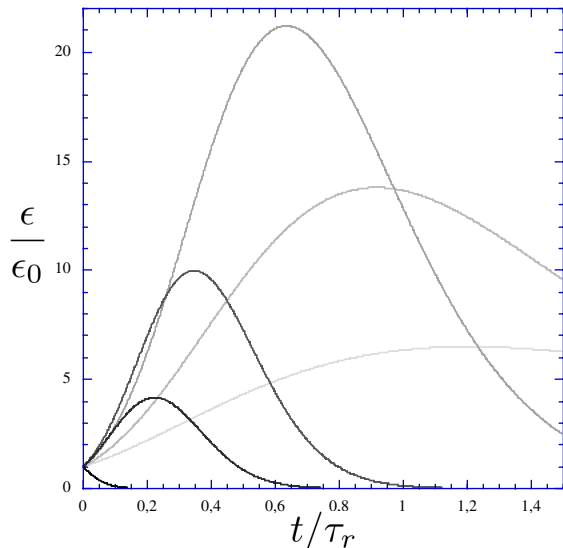
FIG. 3 (color online). Time evolution of the amplitude of the instability at the wave numbers $k = 0.3k_0$ (light gray), $0.4k_0$, $0.53k_0$, $k_0/\sqrt{2}$, $0.8k_0$, and $1.1k_0$ (black), for $\tau_r/\tau_0 = 15$ and $\Delta = \infty$.

equilibrated melt is given by $D = a^2N/\tau_r$. Therefore, holes can form in a weakly stressed viscoelastic film at the condition that h_0 is smaller than $a(N/P)^2$. Note that this length is much larger than the size R of a relaxed chain. Most interestingly, the higher the molecular weight of the polymer the more a thin film is subject to instabilities. This result resolves the apparent contradiction between the experimental results of Reiter et al. [8,9] and the predictions of Safran and Klein [7]. The condition $h_0 \ll a(N/P)^2$ is indeed satisfied in the experiments presented in [8,9,13] [$a(N/P)^2$ spans between 450 nm and 125 μm, while h_0 spans between 20 nm and 200 nm]. Note that the thinner the film, the smaller the minimum stress necessary to cause a rupture of the film.

In conclusion, we have shown that a small stress ($|\sigma_0|/G > \sqrt{\gamma/bG}$) always amplifies thickness fluctuations in thin viscoelastic films, similarly to a spinodal process. However, these fluctuations will not all result in the appearance of holes because of the relaxation time of the stress. Holes will only form from large enough thickness fluctuations [$\epsilon_0 \gtrsim \exp(-0.4\tau_r/\tau_0)$], similarly to what is observed with an heterogeneous instability process. Since τ_r/τ_0 increases with the stress σ_0, the number density of appearing holes increases with the stress, whatever the thickness variation distribution, giving a theoretical support to experimental observations [8,9]. The rate τ_r/τ_0 is also a decreasing function of h_0, which implies that the holes density increases when decreasing the film thickness, as always observed. Most importantly, the increase of τ_r/τ_0 with the molecular weight of the polymer explains the counterintuitive observation of an increase of the holes density with the molecular weight [10].

An interesting result is that there cannot be any spatial coherence between holes on length scales larger than $\Delta = \sqrt{h_0b}$ because of the friction of the film on the substrate, in agreement with the observations of Jacobs et al. [13] and Reiter et al. in [9].

Note that, for the sake of simplicity, we have left the disjoining pressure out of the present study. In most current experimental cases, the latter will also contribute to the growth of the instability. Other sources of instability such as density defects may also be involved in the rupture of polymer films [6,13].

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