

Dynamics of a thin liquid film with surface rigidity and spontaneous curvature

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(Received 11 January 2011; published 25 April 2011)

The effect of rigid surfaces on the dynamics of thin liquid films that are amenable to the lubrication approximation is considered. It is shown that the Helfrich energy of the layer gives rise to additional terms in the time-evolution equations of the liquid film. The dynamics is found to depend on the absolute value of the spontaneous curvature, irrespective of its sign. Due to the additional terms, the effective surface-tension can be negative and an instability at intermediate wavelengths is observed. Furthermore, the dependence of the shape of a droplet on the bending rigidity as well as on the spontaneous curvature is discussed.

DOI: [10.1103/PhysRevE.83.040601](https://doi.org/10.1103/PhysRevE.83.040601)

PACS number(s): 68.15.+e, 87.16.D-, 47.20.Dr, 68.03.Cd

I. INTRODUCTION

Surfactant monolayers and multilayers at a free interface, which are most commonly formed by lipid molecules, exhibit extremely rich phase diagrams with an abundance of different ordering states [1,2]. In addition to their fascinating thermodynamics, they have been intensively studied as model systems for biological membranes that are composed of phospholipid bilayers [3]. Furthermore, floating surfactant layers are important for technical applications as they can be transferred onto solid substrates utilizing, e.g., Langmuir-Blodgett transfer, allowing for a controlled coating with an arbitrary number of molecular layers and even for the self-organized nanopatterning of surfaces [4–7].

Depending on the chemical and thermodynamic properties of the used material, surfactant monolayers and multilayers are rigid to some extent. The consequences are twofold: On the one hand, the layer has a certain bending rigidity, so that additional work has to be surmounted in order to deform the surface. This bending rigidity is measurable by x-ray scattering and depends strongly on the surfactant material and the thermodynamic phase of the layer [8,9]. On the other hand, the layer can exhibit spontaneous curvature due to different chemical properties of the head groups and tail groups of the surfactant molecules [10].

One can expect these effects to be even more pronounced if the liquid support of such a surfactant layer becomes a very thin film, as is the case, for example, in coating processes, so that interfacial influences become increasingly important. The dynamics and the stability of thin liquid films have been studied experimentally and theoretically in recent years (see the reviews in Refs. [11,12]). Theoretically, it is accurately described within the framework of the lubrication approximation, which has been used extensively throughout the literature to describe films covered with layers of soluble and insoluble surfactants [13–15]. However, the focus of these investigations has been on the effect of surfactant-induced surface-tension gradients or on monolayer thermodynamics, whereas surface rigidity is commonly neglected. It is the purpose of the present paper to generalize the lubrication approximation of thin liquid

films in this respect by incorporation of the bending rigidity and the spontaneous curvature of a surface layer. Following this approach, we find that the surface rigidity gives rise to a pair of antagonistic effects: While short-wavelength fluctuations are suppressed by the bending rigidity, the spontaneous curvature can lead to instabilities at intermediate wavelengths.

II. THIN LIQUID FILMS WITH RIGID SURFACE LAYERS

In the spirit of Helfrich, the energy of a rigid interfacial layer can be written as the sum of integrals over the mean curvature and the Gaussian curvature of the surface [10,16]. According to the Gauss-Bonnet theorem, the latter integral is a topological quantity, dependent only on the genus p of the considered surface S . With the denotation of the principal curvatures of S by κ_1 and κ_2 and the spontaneous curvature by κ_0 , the energy E_r due to the rigidity of a surface S is accordingly obtained as

$$E_r = \frac{k_c}{2} \int dS (\kappa_1 + \kappa_2 - \kappa_0)^2 + 2\pi k_g (1 - p). \quad (1)$$

The positive material constants k_c and k_g are the bending rigidity and the modulus of the Gaussian curvature, respectively. Here we focus on thin films that are entirely covered by a homogeneous surfactant layer without defects, that is, the case of constant surface topology. If the liquid film is described by its height profile $h(\mathbf{x}, t)$ as shown in Fig. 1, the Helfrich energy can be written as a functional $E_r = E_r[h]$.

In equilibrium there must be a balance of forces $\delta W = 0$ at the surface, where

$$\delta W = \int dx \int dy \delta h \left(p - \sigma(\kappa_1 + \kappa_2) - \pi_d + \frac{\delta E_r}{\delta h} \right). \quad (2)$$

Here σ is the surface tension, p is the pressure in the liquid phase, and π_d denotes the disjoining pressure describing the interaction between the substrate and liquid, which must be taken into account for very thin films. To calculate the functional derivative of E_r we use the fact that one can rewrite the mean curvature as $\kappa_1 + \kappa_2 = -\nabla \cdot \hat{\mathbf{n}}$, where

$$\hat{\mathbf{n}} = \frac{1}{a^{1/2}} \begin{pmatrix} -\partial_x h \\ -\partial_y h \\ 1 \end{pmatrix} \quad \text{for } a = 1 + (\nabla h)^2$$

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is the unit normal of the water surface, pointing into the vapor phase. We find

$$\begin{aligned} \frac{\delta E_r}{\delta h} = & k_c \nabla \cdot \left\{ (\nabla \cdot \hat{\mathbf{n}} + \kappa_0) \left[a^{1/2} \left(\nabla \cdot \frac{\hat{\mathbf{n}}}{a} \right) (\nabla h) \right. \right. \\ & \left. \left. + \frac{2(\nabla^2 h) \hat{\mathbf{n}} - (\nabla \cdot \hat{\mathbf{n}} + \kappa_0)(\nabla h)}{2a^{1/2}} - \frac{(\nabla h)(\nabla^2 h)}{a} \right] \right. \\ & \left. - \nabla [a^{-1}(\nabla \cdot \hat{\mathbf{n}} + \kappa_0)] \right\}. \end{aligned} \quad (3)$$

By introducing the scales h_0 , l_0 , and t_0 for height, length, and time, one can derive the time-evolution equation for the nondimensionalized height profile $H(\mathbf{X}, T) \equiv h(\mathbf{X} l_0, T t_0)/h_0$ within the lubrication approximation. To this end, we follow precisely the steps in Sec. II B of the derivation by Oron *et al.* [11], with the difference that our force balance equation contains the additional contribution $\delta E_r/\delta h$. By expanding the functional derivative [Eq. (3)] in powers of the parameter $\epsilon = h_0/l_0$, which is small for thin liquid films, one obtains, up to order ϵ^3 ,

$$\begin{aligned} \frac{\delta E_r}{\delta h} = & \frac{k_c}{2} \nabla \cdot \left[\frac{2\epsilon}{l_0^3} \nabla \nabla^2 H - \frac{\epsilon \kappa_0^2}{l_0} \nabla H \right. \\ & - \frac{4\epsilon^2 \kappa_0}{l_0^2} \left((\nabla^2 H) \nabla H - \frac{1}{2} \nabla (\nabla H)^2 \right) \\ & + \frac{5\epsilon^3}{l_0^3} (\nabla^2 H)^2 \nabla H \\ & \left. - \frac{\epsilon^3}{l_0^3} \nabla [3(\nabla^2 H)(\nabla H)^2 + 2(\nabla H) \cdot \nabla (\nabla H)^2] \right]. \end{aligned}$$

By inserting this result into the force balance equation [Eq. (2)] and expanding the remaining terms in powers of ϵ as well, we obtain, after dropping terms of higher orders in ϵ , the following formula, which is a generalization of Eq. (2.24b) in Ref. [11]:

$$-P + \Pi = \bar{C}_I^{-1} \nabla^2 H + \bar{C}_{II}^{-1} \nabla^4 H,$$

where $P = \epsilon h_0 p/\mu U_0$ and $\Pi = \epsilon h_0 \pi_d/\mu U_0$ with characteristic velocity $U_0 = l_0/t_0$ are the nondimensionalized pressure and disjoining pressure and

$$\bar{C}_I^{-1} = \frac{\epsilon^3}{U_0 \mu} \left(\sigma - \frac{k_c \kappa_0^2}{2} \right), \quad \bar{C}_{II}^{-1} = \frac{\epsilon^3}{U_0 \mu} \frac{k_c}{2l_0^2}. \quad (4)$$

With this result at hand, one can follow the remaining steps of the standard derivation in Ref. [11] to obtain the time-evolution equation

$$\partial_T H = -\nabla \cdot \left(\frac{H^3}{3} \nabla [\bar{C}_I^{-1} \nabla^2 H - \bar{C}_{II}^{-1} \nabla^4 H - \Pi(H)] \right). \quad (5)$$

It is a noteworthy result that the thin-film dynamics depends not on the sign of the spontaneous curvature but only on its absolute value.

Typical values for the bending modulus and the spontaneous curvature are $k_c \approx 10^{-19}$ J [8,9] and $|\kappa_0| \approx 10^7$ – 10^9 m $^{-1}$ [17], respectively. One can thus roughly estimate $k_c \kappa_0^2/2 \approx 10^{-5}$ – 10^{-1} J/m 2 . By comparing this range of values to the surface tension of water in the absence of any surfactant, $\sigma_{\text{abs}} \approx 72 \times 10^{-2}$ J/m 2 , we note that the contribution due to spontaneous

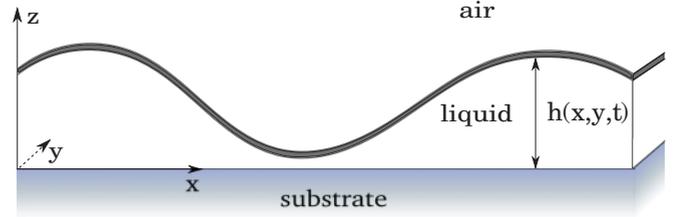


FIG. 1. (Color online) Schematic drawing of a thin liquid film with a rigid surface layer. The shape of the film is described by its height profile $h(\mathbf{x}, t)$, which gives the film thickness above point \mathbf{x} at time t .

curvature can be of the same order of magnitude or even larger. The latter implies that spontaneous curvature can lead to a negative effective surface tension. By assuming $l_0 \approx 10^{-7}$ – 10^{-6} m one can further estimate $k_c/2l_0^2 \approx 10^{-7}$ – 10^{-5} J/m 2 . Thus \bar{C}_{II}^{-1} will, in most cases, be orders of magnitude smaller than \bar{C}_I^{-1} .

III. LINEAR STABILITY OF FLAT FILMS

Any homogeneous film profile $H(\mathbf{X}, T) = \hat{H} = \text{const}$ solves Eq. (5). In the consideration of small perturbations $\eta(\mathbf{X}, T)$ of a flat film, we insert $H(\mathbf{X}, T) = \hat{H} + \eta(\mathbf{X}, T)$ into Eq. (5) and keep only terms linear in η . By using the plane-wave ansatz $\eta \sim \exp(i\mathbf{k} \cdot \mathbf{X} + \lambda T)$ the dispersion relation $\lambda(k)$ is obtained as

$$\lambda(k) = -\frac{\hat{H}^3}{3} k^2 (\hat{\Pi}' + \bar{C}_I^{-1} k^2 + \bar{C}_{II}^{-1} k^4), \quad (6)$$

where we use the shorthand notation $\hat{\Pi}' \equiv \partial_H \Pi(H)|_{H=\hat{H}}$ and $k \equiv |\mathbf{k}|$.

This result complies with the physical intuition that for vanishing spontaneous curvature the bending rigidity will damp short-wavelength fluctuations and thus has a stabilizing influence. However, if \bar{C}_I^{-1} takes negative values, this can lead to an instability for intermediate wave numbers: For $\bar{C}_I^{-1} < 0$ and $\hat{\Pi}' = \bar{C}_I^{-2}/4\bar{C}_{II}^{-1}$ the eigenvalue $\lambda(k_{\text{cr}})$ of the mode $k_{\text{cr}} = \sqrt{-\bar{C}_I^{-1}/2\bar{C}_{II}^{-1}}$ crosses the imaginary axis (solid

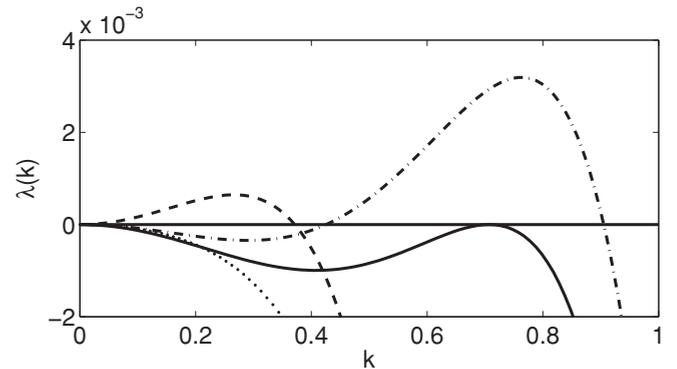


FIG. 2. Dispersion relation $\lambda(k)$ [see Eq. (6)] for four different parameter sets: $\bar{C}_I^{-1} = -0.1$, $\bar{C}_{II}^{-1} = 0.1$, and $\hat{\Pi}' = 0.025$ (solid line); $\bar{C}_I^{-1} = -0.1$, $\bar{C}_{II}^{-1} = 0.1$, and $\hat{\Pi}' = 0.0148$ (dash-dotted line); $\bar{C}_I^{-1} = 0.1$, $\bar{C}_{II}^{-1} = 0.1$, and $\hat{\Pi}' = -0.0157$ (dashed line); and $\bar{C}_I^{-1} = 0.1$, $\bar{C}_{II}^{-1} = 0.1$, and $\hat{\Pi}' = 0.0148$ (dotted line).

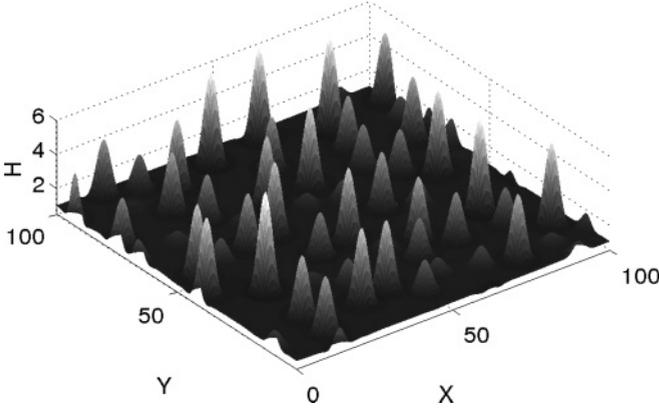


FIG. 3. Snapshot of a numerical simulation of the breakup of a homogeneous film with $\hat{H} = 1.2$, $\bar{C}_I^{-1} = -0.1$, and $\bar{C}_{II}^{-1} = 0.1$.

line in Fig. 2), so that for $0 < \hat{\Pi}' < \bar{C}_I^{-2}/4\bar{C}_{II}^{-1}$ and $\bar{C}_I^{-1} < 0$ there is a band of unstable modes $k_1 < k < k_2$ (dash-dotted line in Fig. 2) with

$$k_{1,2} = \sqrt{\frac{-\bar{C}_I^{-1} \mp \sqrt{\bar{C}_I^{-2} - 4\bar{C}_{II}^{-1}\hat{\Pi}'}}{2\bar{C}_{II}^{-1}}}.$$

Obviously $k_1 = 0$ for negative $\hat{\Pi}'$ and arbitrary values of \bar{C}_I^{-1} (dashed line in Fig. 2). The wave number k_{\max} corresponding to the maximum of $\lambda(k)$, that is, the most unstable mode, is given by

$$k_{\max} = \sqrt{\frac{-\bar{C}_I^{-1} + \sqrt{\bar{C}_I^{-2} - 3\bar{C}_{II}^{-1}\hat{\Pi}'}}{3\bar{C}_{II}^{-1}}}$$

with

$$\lambda(k_{\max}) = -\frac{\hat{H}^3 \left(-\bar{C}_I^{-1} + \sqrt{\bar{C}_I^{-2} - 3\bar{C}_{II}^{-1}\hat{\Pi}'} \right)}{81\bar{C}_{II}^{-2}} \times \left(6\bar{C}_{II}^{-1}\hat{\Pi}' - \bar{C}_I^{-2} + \bar{C}_I^{-1}\sqrt{\bar{C}_I^{-2} - 3\bar{C}_{II}^{-1}\hat{\Pi}'} \right).$$

For $\hat{\Pi} > 0$, $\bar{C}_I^{-1} > 0$, and $\bar{C}_{II}^{-1} > 0$, the whole spectrum is damped (dotted line in Fig. 2).

A numerical simulation [18] of a randomly perturbed flat film of height $\hat{H} = 1.2$ with $\bar{C}_I^{-1} = -0.1$ and $\bar{C}_{II}^{-1} = 0.1$ was carried out using the disjoining pressure $\Pi(H) = AH^{-3}(1 - H^{-3})$ with the Hamaker constant $A = 6.5 \times 10^{-2}$. Here the scale h_0 is set equal to the equilibrium adsorbed layer so that $\Pi(1) = 0$. The simulated situation corresponds precisely to the dash-dotted line in Fig. 2. The flat film quickly breaks up into small droplets, which then undergo a process of coarsening, as is commonly observed after film rupture, as is commonly observed after film rupture (see Fig. 3). It should be noted that, due to the repulsive component in our specific choice of Π , a complete rupture occurs not to $H = 0$, but only to a macroscopically dry substrate with $H = 1$. However, the above stability analysis is valid for arbitrary disjoining pressures. Remarkably, our results predict that rigid layers with spontaneous curvature can be used to destabilize very thin films, which would remain flat in the absence of the surfactant

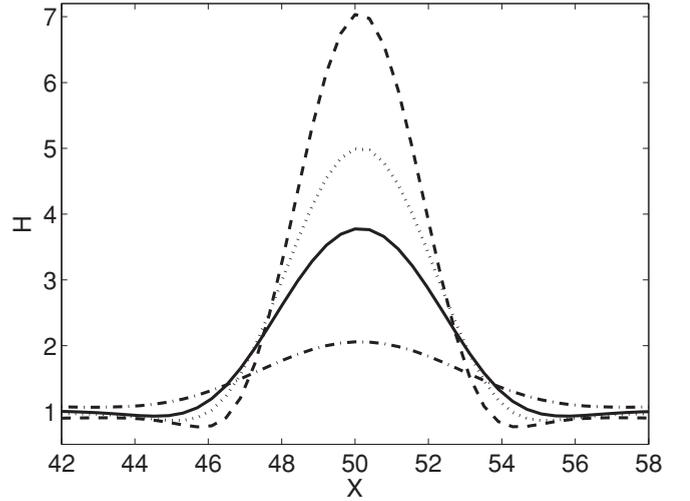


FIG. 4. Different shapes of a droplet obtained for $\bar{C}_{II}^{-1} = 0.1$ and $\bar{C}_I^{-1} = 0$ (dash-dotted line), $\bar{C}_I^{-1} = -0.05$ (solid line), $\bar{C}_I^{-1} = -0.07$ (dotted line), and $\bar{C}_I^{-1} = -0.1$ (dashed line). The image shows a closeup of a steady state on a periodic domain of size $L = 100$.

layer, and to obtain droplets of extremely small volumes after film breakup.

IV. THE SHAPE OF A DROP COVERED WITH A RIGID LAYER

It was shown in the preceding section that surface rigidity affects the linear stability of flat films. Now we investigate how the rigidity affects the shape of the droplets that are formed during the rupture of an unstable film. To this end we consider the steady-state solutions of Eq. (5), which were obtained by relaxation, on a one-dimensional domain, that is, direct numerical integration of Eq. (5). When a steady state is obtained for one set of parameters, it is used as the initial condition for the subsequent run. Thus the overall volume of liquid within the integration domain is constant throughout a whole parameter scan.

First $\bar{C}_{II}^{-1} = 0.1$ is held constant while \bar{C}_I^{-1} is varied from 0 to -0.1 . The shape of the droplet obtained depends sensitively on \bar{C}_I^{-1} , as shown in Fig. 4. The drop becomes steeper and develops more and more pronounced undershoots below the precursor height $H = 1$ as the parameter is decreased.

In a second parameter scan $\bar{C}_I^{-1} = 0.1$ is fixed while \bar{C}_{II}^{-1} is varied from 0 to 50, as shown in Fig. 5. The results indicate that the scaled bending modulus $k_c/2l_0^2$ needs to be 10–100 times higher than the effective surface tension in order to change the shape of the droplet significantly.

V. CONCLUSIONS AND OUTLOOK

A generalization of the equations of thin-film flow to the case of rigid surface layers with spontaneous curvature has been presented. Our results show that the spontaneous curvature can lead to a significantly lower and even negative effective surface tension, resulting in the breakup of very thin flat films. In the case of negative \bar{C}_I^{-1} and positive \bar{C}_{II}^{-1} the instability occurs at a finite wavelength, while the $k = 0$

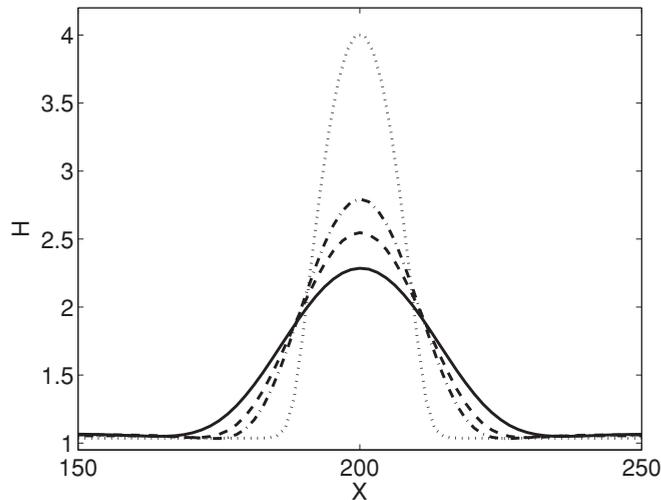


FIG. 5. Different shapes of a droplet obtained for $\bar{C}_I^{-1} = 0.1$ and $\bar{C}_{II}^{-1} = 0$ (dotted line), $\bar{C}_{II}^{-1} = 10$ (dash-dotted line), $\bar{C}_{II}^{-1} = 30$ (dashed line), and $\bar{C}_{II}^{-1} = 50$ (solid line). The image shows a closeup of a steady state on a periodic domain of size $L = 400$.

mode is neutral due to the conservation law governing the films evolution. It turns out that only the absolute value and not the sign of the spontaneous curvature is important in the lubrication regime.

We have shown that the sensitivity of steady droplet solutions on \bar{C}_{II}^{-1} is very low. Although it is very small in most physical situations, the presence of \bar{C}_{II}^{-1} in the model is crucial because it is necessary to stabilize short-wavelength fluctuations in the case of negative \bar{C}_I^{-1} .

It would be of interest to extend the model further to the case of surfactant layers with evolving topology, that is, to layers that can break up and form holes, leading to contributions $\sim k_g$ to the surface energy. This could also be applicable to binary surface layers consisting of material in two different thermodynamic phases if only one phase has significant rigidity.

ACKNOWLEDGMENTS

This work was supported by the Deutsche Forschungsgemeinschaft within SRF TRR 61.

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