Dynamical Instability of Thin Liquid Films Between Conducting Media

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It is shown that thin dielectric liquid films between electrically conducting media are dynamically unstable if the electronic work functions of the conductors are different. As a consequence, they are expected to dewet by a spinodal dewetting scenario, i.e., via amplification of surface waves with mode selection. The wave number of the fastest growing mode is discussed as a function of the strength of the electric and dispersive forces. In contrast to what seems to be widely believed, it turns out that electric forces dominate over dispersive forces in most experimental situations of the rather general type studied here.

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Structure formation processes in dewetting of thin liquid films have attracted rapidly growing interest in recent years [1–6]. This is due in part to the fundamental interest in the basic interactions and spontaneous symmetry breaking processes involved, but also to the enormous technological relevance of adhesion failure mechanisms of coatings. Therefore, most experimental studies in this field considered thin liquid films on solid substrates at ambient conditions, such that the influence of the adjacent medium (air) on the dynamics and on the driving forces could be safely neglected. However, for simple practical applications like underwater coatings for ships, transatlantic telecommunication cables, or marine oil drilling, it is of great interest to study thin film coatings immersed in a liquid counterphase. Given the abundance of thin film systems between liquid phases in colloid science and biology, the importance of such studies is even clearer. More specifically, the fact that the media adjacent to the film may be electrically conductive (cf. Fig. 1), such as the aqueous phases involved in most of the above-mentioned systems, must be taken into account. As it will be shown below, this may indeed change the dynamical behavior of the film dramatically.

This work was motivated in particular by recent experiments with dielectric liquid films [poly-dimethyl-siloxane (PDMS) and PDMS/polystyrene composite] on silicon substrates, immersed in water [7]. A dynamical instability of the films with mode selection was clearly observed at various conditions. Although the observations could be qualitatively discussed in the framework of dispersion forces, quantitative understanding was not achieved. More specifically, in some cases, Hamaker constants had to be assumed which exceeded the theoretically expected values by more than 2 orders of magnitude [8]. The present work thus explores the dynamical stability of dielectric liquid films between two electrically conducting counterphases. It turns out that these films exhibit, quite generally, an instability driven by the electric field which builds up across the film due to the difference of the electronic work functions of the adjacent media. This leads to the amplification of thermal surfaces waves (or initial inhomogeneities in film thickness) and comprises strong mode selection. The resulting scenario may be considered as a variant of spinodal dewetting [6], but with much stronger driving forces than those arising from van der Waals (i.e., dispersive) interactions. In future analysis of experimental work involving liquid films between conducting media, the effect discussed here must be taken into account.

The equation of motion for the lateral liquid flow in a thin film may be readily obtained from the continuity equation (assuming incompressibility of the liquid),

$$\frac{\partial}{\partial t} h(x,t) = -\frac{\partial}{\partial x} j(x,t) = C\frac{\partial^2}{\partial x^2} p[h(x,t)], \tag{1}$$

where x is the lateral coordinate, $h(x,t)$ is the local film thickness, and $j(x,t)$ is the lateral liquid flow in the film, integrated along the normal coordinate. The shape of the flow profile and the viscosity of the liquid are absorbed into the positive constant C. $p(x,t)$ is the film pressure, which can be written as

$$p = \frac{A}{6\pi h^3} + \frac{\epsilon\epsilon_0 U^2}{2h^2} - \sigma\frac{\partial^2 h}{\partial x^2}. \tag{2}$$

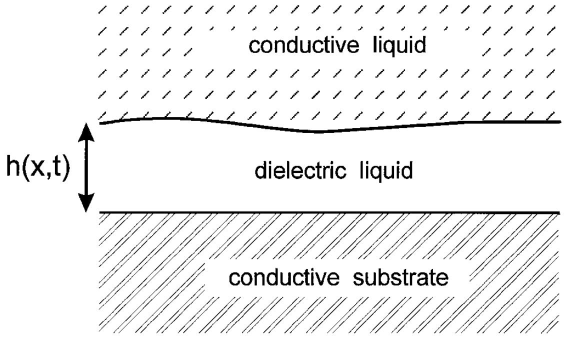

FIG. 1. The system under consideration: a dielectric (nonconductive) liquid film on a solid conductor, immersed in a conductive liquid (e.g., water).

The first term is the disjoining pressure in the film, with A the Hamaker constant describing the van der Waals interaction of the film with the surrounding media. The second term represents the electrostatic pressure exerted on the film by an electrostatic potential difference, U, between the conducting media cladding the film, with ϵ being the dielectric constant of the film material. Finally, the third term describes the Laplace pressure in the film, with σ denoting the interface tension between the film and the upper (liquid) medium [9].

Let us rest for a while with the quantity U introduced here. Consider a liquid film which is thin enough for van der Waals forces to have to be included, i.e., whose thickness is well below 1 μm. For all practical purposes, it can be safely assumed that such a film will not be free of defects, be it a (more or less conducting) dust particle or a pinhole at which an electron exchange between the conducting half spaces cladding the film may take place. This leads to an electric potential difference, U, which is equal to the difference in the electronic work functions of the conductors. Away from the defects, *the film will thus be subject to an electric field, U/h, which is fully determined by the film thickness and the work functions of the two conducting media.* The incorporation of the second term in Eq. (2) is thus a necessity for the system under study.

Let us now consider the fate of small fluctuations of the thickness of an initially homogeneous film of thickness h_0. Inserting Eq. (2) into Eq. (1), and keeping only terms linear in the amplitude of the fluctuations, we readily obtain

$$-C^{-1}\frac{\partial h}{\partial t} = \left(\frac{A}{2\pi h_0^4} + \frac{\epsilon\epsilon_0 U^2}{h_0^3}\right)\frac{\partial^2 h}{\partial x^2} + \sigma\,\frac{\partial^4 h}{\partial x^4}\,. \qquad (3)$$

Here we have made the important assumption that U is strictly constant. This is justified if the fluctuations of the film are slow enough for the charges in the adjacent media to follow instantaneously. Indeed, due to the small thickness of the film, the lateral flow in the film provides the bottleneck for the dynamics, and charge equilibration in the adjacent conductors can be assumed to be fast enough, even for ionic conductors such as aqueous solutions.

A mode analysis ansatz, $h(x,t) = h_0 + \delta\cos(qx) \times \exp(t/\tau)$, yields the growth rate, $\tau^{-1}(q)$, of the mode with wave number q,

$$(C\tau)^{-1} = \left(\frac{A}{2\pi h_0^4} + \frac{\epsilon\epsilon_0 U^2}{h_0^3}\right)q^2 - \sigma q^4, \qquad (4)$$

from which the mode selection behavior is easily derived. For the wave number of the mode the amplitude of which grows fastest, $q_{\max}$, one immediately obtains

$$q_{\max}^2 = \frac{A}{4\pi\sigma h_0^4} + \frac{\epsilon\epsilon_0 U^2}{2\sigma h_0^3}\,. \qquad (5)$$

In close analogy to spinodal dewetting, one expects an undulative dewetting pattern to evolve with a clearly visible characteristic wavelength equal to $2\pi/q_{\max}$ [3,5,6]. For zero voltage, we have $q_{\max} = \sqrt{A/4\pi\sigma}\,h_0^{-2}$, which is the well-known result for spinodal dewetting by "destabilizing" van der Waals forces (positive A). If, however, the electric force dominates, $q_{\max} = U\sqrt{\epsilon\epsilon_0/2\sigma}\,h_0^{-3/2}$. In fact, this should be usually the case, as one sees immediately if one puts in reasonable numbers. Typical contact potentials are on the order of 1 V. Hamaker constants are on the order of 10^{-20} J [10]. Consequently, at a film thickness of 100 nanometers, the electric term exceeds the van der Waals term by 3 orders of magnitude.

Let us discuss the interplay of the electric and van der Waals forces in some more detail. There are two natural length scales in the system. One is the well-known parameter $a = \sqrt{|A|/4\pi\sigma}$, which is on the order of a nanometer and appears in the theory of spinodal dewetting by van der Waals forces [11,12]. The other, $\xi = |A|/2\pi\epsilon\epsilon_0 U^2$ is directly connected to the relative strength of dispersive and electric forces. Inserting the above numbers, one obtains $\xi \approx 0.1$ nm. By defining $Q = a/\xi^2$ and $l = h_0/\xi$, we can rewrite Eq. (5) in "dimensionless" form as

$$q_{\max}^2 = Q^2(l^{-3} \pm l^{-4})\,. \qquad (6)$$

The sign of the l^{-4} term is to be taken as the same as the sign of A. In Fig. 2, $q_{\max}^2(l)$ is plotted for both cases, the dashed line representing positive A (destabilizing van der Waals forces), and the solid line representing negative A (stabilizing van der Waals forces). In the latter case, films with $h_0 < \xi$ are dynamically stable.

For most applications of the model, l will be much larger than 1, such that the dispersive contributions may be neglected, and $q_{\max} \propto h_0^{-3/2}$. The dependence of the characteristic length scale of the dewetting pattern on

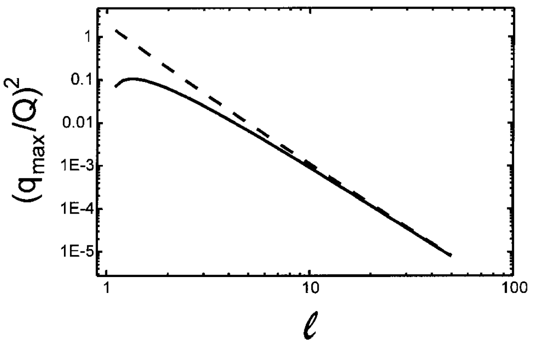

FIG. 2. The wave number of the fastest growing mode vs the reduced film thickness, l. Dashed line, positive Hamaker constant (destabilizing van der Waals forces). Solid line, negative Hamaker constant (stabilizing van der Waals forces). In the latter case, films with $|l| < 1$ are dynamically stable.

system parameters such as the film thickness and the electronic work functions may be used to clearly identify the scenario described here from dispersion force driven spinodal dewetting. It should be noted that in most colloidal systems, where the conductors adjacent to the film usually are aqueous solutions, the work function differences are typically on the order of 10 mV. In this case, ξ is on the order of 1 μm such that the dynamical instability develops very slowly due to the weakness of the destabilizing forces, and may be hard to observe.

It should finally be mentioned that Eq. (6) applies only if the screening lengths in the adjacent phases are small compared to the film thickness. If this is not the case, a more complicated behavior is to be expected. More specifically, it is straightforward to show that the voltage entering in Eq. (2) is to be replaced by $V = U/(1 + L/h)$, with L representing the sum of the screening lengths in the two phases cladding the film. We then have

$$p = \frac{A}{6\pi h^3} + \frac{\epsilon\epsilon_0 U^2}{2(L + h)^2} - \sigma\frac{\partial^2 h}{\partial x^2}, \tag{7}$$

which is to be replaced in all further equations. As a consequence, since L is positive, the dependence of $q_{\max}$ upon l is weaker than with $L = 0$.

If the dispersion forces tend to stabilize the film ($A < 0$), we can directly derive a stability criterion for the film from Eq. (7). We obtain

$$\frac{L}{\xi} > l^{4/3} - l, \tag{8}$$

which is plotted in Fig. 3. It clearly demonstrates the stabilizing action of the finite screening in the adjacent conductors upon the film. However, for any screening length, there is obviously a finite thickness above which the film becomes inevitably unstable.

In conclusion, the present work predicts a dynamical instability of dielectric coatings between electrically conducting media which is expected to occur quite universally and should play an important role for many systems with practical applications. It is to be expected that the results presented here will cast a new light on a number of effects which have been already observed, but remained unexplained.

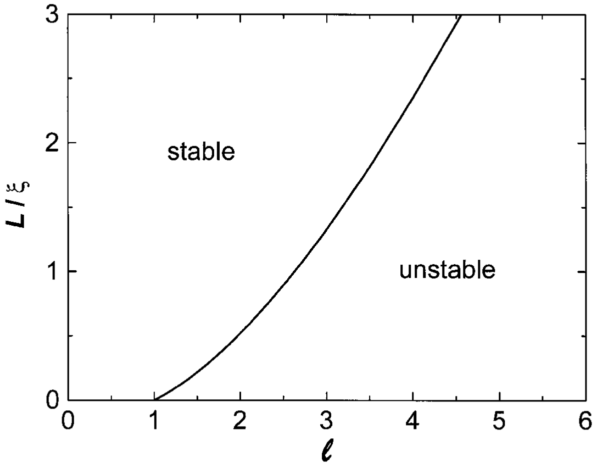

FIG. 3. The effect of the screening length in the adjacent conductors on the film stability. Although the film becomes more stable when the screening length is larger, there is always a finite thickness above which the film becomes unstable.

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