Nucleation/Nucléation

Dewetting through nucleation

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Abstract

We review some fundamental aspects of nucleation processes occurring in dewetting phenomena. We elaborate on the analogy between dewetting scenarios and nucleation in bulk systems. While this analogy may be pushed quite far in a few systems, fundamental differences arise in many cases of common interest. We present a number of examples and discuss their relevance in real situations. ***To cite this article: S. Herminghaus, F. Brochard, C. R. Physique 7 (2006).***

Résumé

Démouillage et nucléation. Nous passons en revue quelques aspects fondamentaux des processus de nucléation qui se produisent lors des phénomènes de démouillage. Nous développons l'analogie entre les scénarios de démouillage et la nucléation en volume. Alors que cette analogie peut être poussée très loin dans certains systèmes, des différences apparaissent dans beaucoup de cas usuels. Nous présentons plusieurs exemples et nous discutons leur application à des situations réelles. ***Pour citer cet article : S. Herminghaus, F. Brochard, C. R. Physique 7 (2006).***

There are many situations in which two materials are separated by a thin liquid film. The spatially closest example is, very probably, the tear film coating your eyeball, which protects the delicate tissue of the cornea from the surrounding air. Other examples are the oil film between the pan and the steak, the lubricant on the hard disk drive, a thin coating of paint or lacquer, or a soap film in a froth, separating two adjacent air bubbles. The thickness of such films varies over several orders of magnitude, from molecular thickness in lubricant films up to millimeter range in paint films or in aquaplaning situations. In the present article, we review a few fundamental aspects concerning the stability of these films, with emphasis on nucleation phenomena. For the sake of clarity, but without loss of generality, we will mainly discuss liquid films coating a solid substrate. Generalization to other situations is straightforward, and in most aspects quite obvious.

In order to appreciate the relevance of the stability problem, imagine you try to coat a plastic surface, like an overhead transparency, with a water film by wiping it with a wet sponge. This will clearly not be successful, as the water will not form a homogeneous film, but rather collect in a number of individual droplets. As a result, most of the substrate will turn out dry: dewetting has taken place. Obviously, the dry substrate surface is energetically

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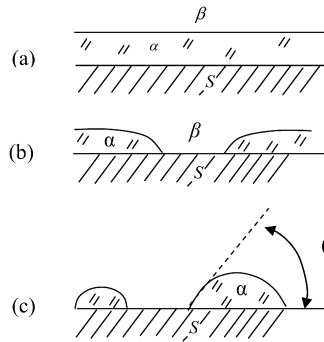
Fig. 1. Schematic representation of the type of systems considered in the present paper. If the homogeneous thick film (a) does not represent the global minimum of the free energy of the system ($S < 0$), dewetting may take place through the formation of a dry patch (b) which grows until all forces are balanced.

more favorable than a homogeneous water film would be. If we denote the substrate by s, the liquid by α, and the surrounding phase (air, in our example) by β (cf. Fig. 1), furthermore the excess free energies per unit area of the corresponding interfaces by $\gamma_{s\alpha}$, $\gamma_{s\beta}$, and $\gamma_{\alpha\beta}$, we can put this in more formal terms by saying that $\gamma_{s\alpha} + \gamma_{\alpha\beta} > \gamma_{s\beta}$, since a (thick) layer of water comprises the s/α and the α/β interface[2] (Fig. 1(a)). Introducing the spreading parameter, $S := \gamma_{s\beta} - (\gamma_{\alpha\beta} + \gamma_{s\alpha})$, which quantifies the tendency of the liquid to wet the substrate surface in the presence of β, we may write as well $S < 0$ to characterize the water film as being not stable on the substrate we have chosen. It is clear that such situations are undesirable in most practical cases, and it is of great interest to study the physics of dewetting in some depth.

Before we discuss the stability aspects of the liquid film, let us first take a look at the situation which remains after dewetting is accomplished (Fig. 1(c)). On the substrate, we will find individual droplets which form a characteristic angle with the substrate at their perimeter. This angle is known as Young's angle, θ, and is determined by the force balance at the three-phase contact line where s, α, and β meet. One readily finds the Young–Dupre equation [1],

$$\gamma \cos\theta = \gamma_{s\beta} - \gamma_{s\alpha} \tag{1}$$

where we have used the common short hand $\gamma = \gamma_{\alpha\beta}$ for the surface tension of the liquid. Eq. (1) directly yields the relation $S = \gamma(\cos\theta - 1)$, which is negative for all finite θ. As long as the droplets are small, they represent spherical caps the dimensions of which are determined by their respective volume and by the above constraint of forming Young's angle with the substrate. However, it is clear that large drops will not be spherical: if you spill a glass of water on a substrate with $S < 0$, a flat (i.e., non-spherical) puddle will form, the thickness of which is determined by the balance between gravity and capillarity.

Let us have a closer look at this balance. The excess free energy of the system is given by the integral

$$F\{h(s)\} = \int \left\{ \gamma\left(\sqrt{1 + (\nabla h)^2} - 1\right) + U(h) \right\} \mathrm{d}s \tag{2}$$

where $h(s)$ is the local height of the liquid surface above the substrate, and the integral is extended over the substrate area. $U(h)$ is a suitable potential describing the interaction of the liquid with the substrate and, wherever applicable, with external fields, such as gravity. In order to ease the discussion and make the mathematics more transparent, we will henceforth assume that the contact angle, and accordingly all slopes of the profile, $h(s)$, shall be small as compared to unity, $\theta, h(s) \ll 1$. In this case, we may simply write

$$F\{h(s)\} \approx \int \left\{ \frac{\gamma}{2}(\nabla h)^2 + U(h) \right\} \mathrm{d}s \tag{3}$$

which will be used throughout this paper. Minimalization of F with respect to $h(s)$ yields the Euler–Lagrange equation,

$$\gamma \nabla^2 h = \frac{\mathrm{d}U}{\mathrm{d}h} \tag{4}$$

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[2] As long as all involved materials are thermodynamically stable phases, they do not contribute themselves to this balance.
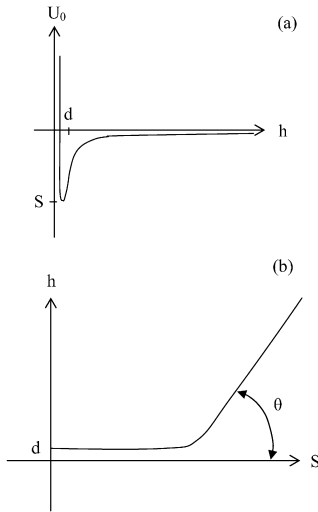
Fig. 2. (a) A typical form of the effective interface potential arising from the molecular scale interactions in a system as the one discussed here. (b) Height profile close to the three-phase contact line due to the potential sketched in (a).
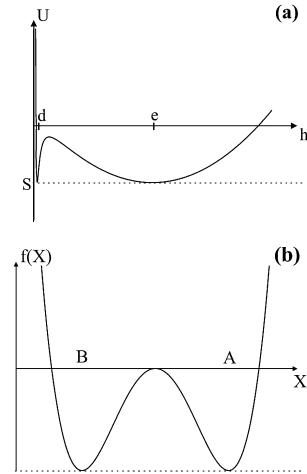
Fig. 3. (a) The effective interface potential for the gravity dominated liquid puddle at equilibrium. Note that both minima are equally deep. (b) Free energy density at coexistence in a bulk system. The abscissa may, for instance, represent the relative concentration in a binary mixture, or the density in a vapor/condensate system.

Applied to the water puddle of our example, this represents the balance between the Laplace pressure of the curved liquid surface (left-hand side of Eq. (4)) and the hydrostatic pressure. The latter is given by $\rho g(e - h)$, where ρ is the density of the liquid, g is the acceleration of gravity, and e is the thickness (*épaisseur*) of the liquid puddle in the homogeneous region. By integration with respect to h, we obtain the gravitational contribution to the potential, $U_g = \frac{\rho g}{2}(h^2 - 2eh)$.

So far, we have not considered the energetics of the three phase contact line. Allowing the film thickness to become arbitrarily small, we can cast the molecular interactions coming into play at short distances into a convenient form by defining the effective interface potential,

$$U_0(h) = f_{\text{film}}(h) - \gamma_{s\alpha} - \gamma \tag{5}$$

were $f_{\text{film}}(h)$ is the free energy per unit area of a homogeneous film of thickness h. Thus, by definition, $U_0 \to 0$ as h becomes large as compared to molecular scale. A typical $U_0(h)$ for a non-wetting system is depicted in Fig. 2(a), the characteristic feature being the global minimum below the h-axis, with a depth $|S|$ at some molecular thickness, $h = d$.[3] Inserting such a shape as $U = U_0$ into Eq. (3), one readily sees that this leads to a profile like that shown in Fig. 2(b), representing the boundary between a molecularly thin adsorption layer of thickness d (where d may well be zero) and a liquid interface making an angle $\theta = \sqrt{2|S|/\gamma}$ with the substrate (from $S = \gamma(\cos\theta - 1) = -\gamma\theta^2/2$). The contact angle and the depth of the global minimum of U_0 are thus closely related.

The potential describing the liquid puddle, on the nonwet substrate in the presence of gravity, is now given by $U = U_0 + U_g$. It is depicted schematically in Fig. 3(a). Since the puddle represents a coexistence between the free substrate (or, respectively, the molecular film of thickness d) and the liquid mesa of thickness e, it is clear that the two minima, at d and at e, must be of equal depth, $S = -\rho g e^2/2$. We thus obtain $e = \theta l_c$, where $l_c = \sqrt{\gamma/\rho g}$ is the capillary length (2.7 mm for water). A puddle of this thickness is stable, and nucleation of a free patch will clearly never occur. We may, however, destabilize the puddle by preparing it in a different way. If we take a bucket of water, immerse the substrate in it, and approach it to the still water surface slowly from below, while keeping it carefully horizontal, we may form a water layer the thickness of which is significantly smaller than the equilibrium puddle thickness. If we now punch a hole in this layer, thus nucleating a free patch of substrate, the patch will grow at

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[3] It should be noted that for positive S (i.e., completely wet systems), care must be taken in defining S, as may be anticipated from the form of U_0 (Fig. 2(a)). This may not concern us here since we exclusively focus on the case $S < 0$.

expense of the area covered with liquid [2]. This will, however, only occur under certain conditions, which will be discussed next.

For illustration and comparison, let us have a glance at nucleation in three-dimensional (i.e., bulk) systems, where it represents a rather clear cut and thoroughly studied problem. If a phase A is in coexistence with another phase, B, the corresponding free energy looks qualitatively as sketched in Fig. 3(b). We may envisage A and B to correspond to different compositions in a binary mixture, or the vapor and liquid density in a simple fluid. Either phase A and B is stable, and if the system is prepared at one of the compositions X_A or X_B, nothing is expected to happen. In contrast, if the system is prepared at some composition, say, slightly below X_A, its free energy density (f_{prep}) is higher than that corresponding to coexistence (f_{coex}) by some amount $\Delta f = f_{prep} - f_{coex}$. It may thus reduce its free energy by forming nuclei of B, which allow the composition in their surrounding to approach X_A. This is analogous to our liquid puddle when the thickness is prepared below the equilibrium thickness. The formation of these nuclei may occur spontaneously by thermal fluctuations, which is called homogeneous nucleation, or by dust particles or other inhomogeneities (called heterogeneous nucleation). A common example is the nucleation of water droplets in super-saturated vapor (A), which leads to the formation of clearly visible clouds, and raindrops (B).[4]

If X lies initially between the inflection points of $f(X)$, where the second derivative of f with respect to X is negative, spinodal decomposition is known to occur, which results in a self-organized pattern of intertwined phases A and B. A similar effect occurs in the dewetting system if the initial film thickness h_0 is chosen such that $d^2U/dh^2 < 0$ [3–6], and has thus been termed spinodal dewetting. However, as Fig. 3(a) suggests, this may be quite delicate to prepare due to the smallness of the region with negative second derivative of U, and in fact has been observed only in few systems, and after extended search [7–9]. Although this is an interesting scenario by itself and important for dewetting, it is somewhat remote from the focus of the present paper and shall not be discussed here any further. The reader is instead referred to the literature [10].

A nucleus of phase B within phase A will grow only if this growth is accompanied by a reduction of the free energy. The latter can be discussed mainly in terms of two quantities: the difference in the bulk free energy densities, Δf, and the excess free energy, γ_{AB}, of the interface between the two phases involved. The total free energy is then, for a spherical nucleus of radius r, given by

$$F(r) = -\frac{4\pi r^3}{3}\Delta f + 4\pi r^2 \gamma_{AB} \qquad (6)$$

It is clear that even if there is a net energy gain for the transformation of A into B, the surface term, which is connected to a smaller exponent of the radius r of the nucleus, always wins for sufficiently small nuclei. There is thus a critical radius r_c which must be reached for the nucleus to be able to grow indefinitely. It is defined by the zero of dF/dr, and is given by $r_c = 2\gamma_{AB}/\Delta f$. The corresponding energy barrier is $F(r_c) = 16\pi\gamma_{AB}^3/3\Delta f^2$. Both r_c and $F(r_c)$ diverge at coexistence, i.e., as Δf goes to zero.

It may be anticipated that the nucleation of a dry patch in a liquid film follows similar rules. In order to discuss the energetics involved, we use the expressions derived above, but introduce a new height coordinate, $\zeta(s) := h(s) - e$, where e is now the initial thickness of the film the stability of which we investigate. This leads to $U_g(\zeta) = \frac{\rho g}{2}(\zeta^2 - e^2)$. Splitting the area of integration in the part of the substrate which is covered by liquid, A, and the dry patch, B, we obtain from Eq. (3)

$$F = \int_A \left\{ \gamma(\nabla\zeta)^2 + U(\zeta) \right\} ds - \int_B S\,ds \qquad (7)$$

Integration by parts yields

$$F = \int_A \left(-\frac{\gamma}{2}\zeta\nabla^2\zeta + U \right) ds + \frac{\gamma}{2}\oint_{\partial A} \zeta(\nabla_\perp\zeta)\,db - \int_B S\,ds \qquad (8)$$

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[4] Heterogeneous nucleation from aerosol particles is known to play a major role in cloud formation.

where ∂A denotes the boundary of A (i.e., the three-phase contact line), and b the corresponding coordinate along that line. Using Eq. (4), we finally obtain

$$F = \int_A \left(\frac{U}{\zeta} - \frac{1}{2} \frac{dU}{d\zeta} \right) \zeta \, ds + \frac{\gamma}{2} \oint_{\partial A} \zeta (\nabla_\perp \zeta) \, db - \int_B S \, ds \tag{9}$$

If we now insert the gravitational potential, $U = U_g$, it turns out that the integrand of the first term vanishes up to a constant, and we find

$$F = -\int_A \frac{\rho g e^2}{2} \, ds + \frac{\gamma}{2} \oint_{\partial A} \zeta (\nabla_\perp \zeta) \, db - \int_B S \, ds \tag{10}$$

Since on the boundary of the patch (∂A) we have $\zeta = -e$ and $\nabla_\perp \zeta = \theta$, furthermore since B is just the complement of A, we may write

$$F = \frac{\gamma}{2} (\kappa^2 e^2 - \theta^2) \mu\{B\} + e\theta \mu\{\partial A\} \tag{11}$$

where we have introduced $\kappa := l_c^{-1}$. $\mu\{B\}$ and $\mu\{\partial A\}$ are the area of the dry patch (i.e., the measure of the set B) and the length of the boundary of that patch, respectively. We have thus arrived at a simple expression which splits the free energy of the opening hole in the film into a contribution from its area, and another one which solely stems from its perimeter. Both depend upon the size, but not on the shape of the patch. In particular, we may now identify the coefficient of $\mu\{\partial A\}$ with the boundary tension, τ_{AB}, i.e., the excess free energy of the boundary between the wet (A) and the dry (B) region. In the particular example of the liquid puddle under gravity, we have $\tau_{AB} = \gamma e\theta/2$.

In order to find the minimal free energy required to form a nucleus of a certain size, we have to consider the most favorable configuration. According to Eq. (11), the circular patch has the smallest free energy among all patches with the same area, since τ_{AB} is positive by assumption. Let us thus imagine a circular dry patch of radius r. Its free energy is

$$F(r) = \frac{\gamma}{2} \left(\pi r^2 (\kappa^2 e^2 - \theta^2) + 2\pi r e\theta \right) \tag{12}$$

If $e < \theta/\kappa$, the first term is negative, and since it will win for large r, it will be favorable for the dry patch to grow and finally remove all liquid from the substrate. For small r, however, the second term dominates, which is always positive. There is thus a maximum in $F(r)$ at the critical radius

$$r_c = \frac{e\theta}{\theta^2 - e^2\kappa^2} \tag{13}$$

which must be overcome for the dry patch to grow by itself, i.e., for $dF/dr < 0$. For $e = \theta/\kappa$, r_c is infinite, and nucleation will not be successful. Just as in bulk nucleation, the energy barrier is also infinite in this case. For small e, it is found to be

$$F(r_c) \approx \frac{\pi}{2} \gamma e^2 \tag{14}$$

Inserting $\gamma \approx 7 \times 10^{-2}$ N/m for water, we see that for thermal nucleation to take place, e would have to be only a few Angstroms. We can thus conclude that thermal (i.e., homogeneous) nucleation plays no noticeable role in dewetting for gravity dominated systems.[5] Nucleation may instead be induced externally, or mediated by some inhomogeneity of the substrate [2].

We shall now discuss the numerical value τ_{AB} in some more detail, since we have so far only included the gravitational contributions. In order to proceed from Eq. (9) to Eq. (10), which was vital for splitting the free energy into an areal and a boundary contribution, we used the special form of $U_g(\zeta)$. If we insert instead $U = U_0 + U_g$, this can not work out in close vicinity of the three-phase contact line, more precisely, in a region with a size comparable to the range of U_0. This is of molecular size, up to a few tens of nanometers if dispersion forces play a dominant role. We are thus left with a residual term which yields an extra excess free energy associated with the three-phase contact line.

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[5] Even for thinner films, it is difficult to observe. It has so far been seen only in liquid Helium coatings [16], in the cyclohexane/methanol system [17] and in thin polystyrene films [10].

In our gravity-dominated example, the region in which the free energy integral contributes to τ_{AB} is very small as compared to the natural length scale of the system, which is given by l_c. On a molecular scale, the three-phase contact line may thus be considered as a straight line, and the integral can be computed directly from U_0, irrespective of the shape of the dry patch. We may thus decompose the total boundary energy into an intrinsic part and a gravitational contribution in an additive way, $\tau_{AB} = \tau_0 + \tau_g$. It has been shown in detail how τ_0 can be obtained analytically from $U_0(h)$ [11]. We should add, however, that τ_0 is of minor relevance here. While $\tau_g = \gamma e \theta / 2 \approx 10^{-5}$ N for the aqueous puddle, τ_0 is of order γ times a molecular length, and hardly ever exceeds 10^{-10} N in a homogeneous system [12].[6]

Up to this point, it may seem that nucleation in dewetting is closely analogous to nucleation in bulk systems. As we have seen, the two terms in Eq. (11) are very much analogous to the free energy density difference (Δf), and the interfacial energy (γ_{AB}), in bulk nucleation. The formal equivalence of Eqs. (12) and (6) is obvious. However, a closer look reveals that this is not generally the case. In fact, the quite imaginative example of the gravity dominated puddle we have discussed above turns out to be one of only a few situations where the analogy can be followed without too much care. As we will show below, the long-range coupling of the substrate surface to the adjacent half space, by virtue of the liquid surface and the non-zero contact angle, renders the concept of the line tension questionable in many cases, since τ_{AB} is found to depend, in general, globally on the size and shape of the nucleus.

Let us see what happens if we turn off gravity in the above example and choose U_0 such as to give no extra contribution to τ_{AB}. This may be achieved with the zero-range potential $U_0(0) = S$ and $U_0(h) = 0 \; \forall h > 0$, such that the intrinsic line tension vanishes ($\tau_0 = 0$) [11]. However, there is still the liquid surface which takes off at the three-phase contact line with a finite contact angle, θ, and which must approach some flat film geometry far away from the dry patch. At zero gravity and in equilibrium, this must be a zero-curvature surface throughout. The corresponding solution for a circular hole of radius r is given by $h(s) = \theta \ln \frac{|s|}{r}$, which represents an 'almost flat' film. Its contribution to the interfacial energy is given by

$$\tau = \int_A \frac{\gamma}{2} (\nabla h)^2 \, ds = 2\pi\theta \int_{|s|>r} \frac{d|s|}{|s|} \tag{15}$$

which is finite only for finite support of $h(s)$, and clearly not localized to the boundary of the dry patch.

One may argue that we have to use a different solution which accommodates a flat film at the perimeter of the sample. This may be achieved by adding a term $\varepsilon|s|^2$ to the above logarithmic profile, where $\varepsilon < 0$ is chosen such as to make the radial derivative vanish at some distance $|s| = R$ far away from the nucleus. This is equivalent to accepting a nonzero (but constant) Laplace pressure around the nucleus, as a consequence of its formation. However, it is readily seen that this does not change the situation qualitatively, since the excess free energy will vary (logarithmically) with R. We see that the excess free energy of a dry patch which arises due to the need of accommodating the three-phase contact at its boundary manifestly depends upon the global geometry of the system, and there is no general way of establishing a well-defined boundary tension.

The physical reason is that there is, at zero gravity, no natural cut-off for the distance over which the substrate is coupled to the adjacent half space. This coupling is characterized by an angle, θ, but not by a length, and is thus of infinite range. The spherical droplets which are found at the end of the dewetting process, as the remains of the liquid film, reflect this fact once more. The size of each droplet, and thus also its maximum height, is solely determined by the contact angle and by its volume, i.e., by its individual history of accumulating liquid from the film during the dewetting process. This reveals another important difference to bulk nucleation phenomena such as those discussed above: there are in most cases not two well-defined minima in the excess free energy corresponding to coexisting 'phases' A and B. While A is initially defined as a film of a certain thickness e, the thickness of the final objects constituting the wet regions is quite arbitrary and depends on the history of the dewetting process.

If, however, the liquid film under discussion is very thin, such that the dispersion forces may noticeably reach through the film, an effective cutoff can be established as well, such that a situation similar to the gravity dominated puddle may arise. For a typical film thickness of 10 nm, the van der Waals pressure is equivalent to about 10^{11} g. In fact, a situation with two equally deep minima of the excess free energy is possible in systems exhibiting a so-called prewetting line [18]. A typical effective interface potential of such systems is depicted in Fig. 4(a).

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[6] There have been reports of much larger line tensions in the last decades, but these were later shown to be due to inhomogeneities in most cases [19].
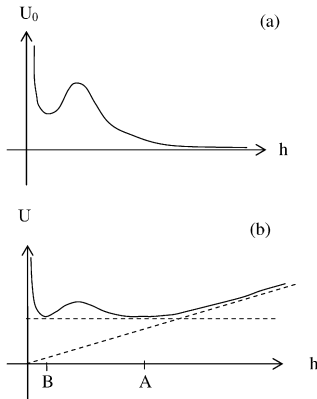
Fig. 4. (a) The effective interface potential of a system which exhibits prewetting. (b) At a certain vapor pressure below saturation, two minima with equal depth arise (solid line). The dotted line indicates the free energy penalty for forming the film material, which arises if the system is off bulk coexistence.
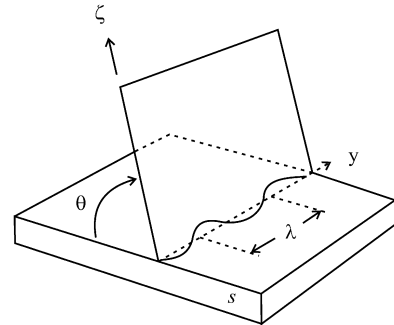

Fig. 5. Sketch of the liquid interface close to the three-phase contact line on a substrate the surface energy of which varies harmonically in space.

If the vapor pressure is slightly below saturation, there is an extra penalty for forming the film, which is proportional to its thickness. This is represented by the dotted line in Fig. 4(b). We thus have $U(h) = U_0 + h\Delta\mu$, where $\Delta\mu$ is the chemical potential difference from saturation. If the latter is chosen accordingly, it is obvious that the two minima of $U(h)$ may have equal depth, representing coexistence of regions with small film thickness (B) with those of the larger thickness (A). Note that this situation is very much analogous to the situation of the gravity dominated puddle.

Since the two minima in Fig. 4 are separated by an intervening maximum, there will accordingly be a certain excess free energy separating regions with the thick film (A) from 'dry' regions, i.e., those with the thin film (B). This will be well defined if the boundary is a straight line, and thus be identified with τ_{AB} for not too strongly curved boundaries. However, if one considers real systems, one finds the critical nucleus is generally so small, and the corresponding curvature of the boundary so large, that the global character of τ_{AB} comes fully into play [13,14]. For practical cases, a separation of contributions as in Eq. (11) is not possible, although in principle, the boundary tension is well defined in this system. Its numerical value is just not relevant for the nucleation problem, due to the small size of the critical nucleus.

There is yet a completely different way of confining the excess free energy contributions to a narrow region close to the three-phase contact line. If the substrate acquires some inhomogeneity, $S = S(s)$, it is clear that the equilibrium contact angle will vary accordingly, $\theta = \theta(s)$. If we assume, as we will do in what follows, that the variations in S, which we call δS are small as compared to S, we have

$$\delta\theta = -\frac{\delta S}{\gamma \sin\theta} \tag{16}$$

Now consider a contact line which is straight at macroscopic scales. Since the liquid interface has to accommodate the spatial variation in the contact angle, as given in Eq. (16) it will have to perform excursions from the usually flat geometry, which introduces some extra energy into the system.

In order to determine this energy, we consider the shape of the liquid interface which is expected to form if there is a harmonic variation of the substrate surface energy. The main idea can be obtained from the sketch displayed in Fig. 5. If we introduce, as an area of reference, the plane representing the asymptote of the liquid interface far away from the three-phase contact line, the deviation of the actual liquid interface away from that plane (measured perpendicularly to the latter) may be represented by

$$\phi = a \sin(qy)e^{-q\xi} \tag{17}$$

the form of which is fixed by the requirement that its Laplacian must vanish, since it must be a zero curvature surface [15]. $q = 2\pi/\lambda$ is the wave number of the inhomogeneity, and a is the amplitude of the deviation, measured in the direction normal to the reference plane. ξ is an auxiliary coordinate measuring the distance away from the (undis-

turbed) three-phase contact line, along the plane of reference. The amplitude is obtained from Eq. (16) by observing that Eq. (17) requires $\delta\theta = aq$. We thus obtain

$$a = -\frac{\delta S_q}{q\gamma \sin\theta} \tag{18}$$

where δS_q is the amplitude of the spatial variation in surface energy at the wave number q.

We furthermore observe that the harmonic excursion does not lead to a change of the projected area of the liquid interface nor of the free substrate surface, since the gain and loss are mutually equal to a very good approximation. We are thus left with the computation of

$$F_{\text{inhomog}} = \frac{\gamma}{2} \iint (\nabla\phi)^2 \, d\xi \, dy \tag{19}$$

as the excess surface free energy created due to the excursion. An important point here is that the exponential in Eq. (17) limits the range over which the inhomogeneity disturbs the liquid surface to a narrow region close to the three-phase contact line. There is thus a chance to arrive at a well-defined, local contribution to the boundary tension, τ_{AB}. From Eq. (17), we see that $(\nabla\phi)^2 = q^2 a^2 e^{-2q\xi}$, which is independent of y. The integral in Eq. (19) is simply $A = qa^2/4$, per unit length of the contact line. In other words, the effective line tension, τ_q, due to a variation of the surface energy with wave number q, is given by

$$\tau_q = \frac{(\delta S_q)^2}{4\gamma q \sin^2\theta} \tag{20}$$

The ubiquity of inhomogeneity on most substrates of practical relevance makes it worthwhile to discuss an illustrative example. Let us assume the variation of the surface energy to come about by the presence of point-like adsorption sites, which are randomly distributed on the substrate surface. One may think of contamination by dust particles. One may as well envisage cell adhesion molecules mediating the adhesion between the plasma membrane of a living cell and the (suitably coated) bottom of a petri dish. Their number density shall be n, and the individual adhesion energy of each binding site will be called E_{bs}.[7] If the distribution is Poissonian, the number density of the binding sites fluctuates spatially in a well defined manner. If we probe substrate regions of some size λ^2, the variation in surface energy is $\delta S = E_{bs}\sqrt{n}/\lambda$. Identifying λ with $2\pi/q$, we obtain from Eq. (20)

$$\tau_q = \frac{E_{bs}^2 nq}{16\pi^2 \gamma \sin^2\theta} \tag{21}$$

It is clear that the largest q which is relevant will be of order $q_{\text{max}} := 2\pi\sqrt{n}$. We may choose to average the contributions over q, with cutoff at q_{max}. This yields

$$\tau_{bs} = \frac{1}{q_{\text{max}}} \int_0^{q_{\text{max}}} \tau_q \, dq = \frac{E_{bs}^2 n^{3/2}}{16\pi \gamma \sin^2\theta} \tag{22}$$

In fact, Fattaccioli has recently reported experiments which showed that vesicles loaded with biotin-streptavidin anchors on a corresponding substrate exhibit a noticeable three-phase contact line tension of the order of magnitude predicted by Eq. (22), with the characteristic monotonic increase with the density of the binding sites [20].

We should discuss the relevance of such inhomogeneity contributions to the boundary tension in connection with the nucleation problem, i.e., its relevance for the size of the critical nucleus. To this end we return to the more general expression, Eq. (20). For the critical radius in the case $\tau_{AB} = \tau_q$, we obtain $2\pi r_c \tau \approx \pi r^2 S$. We thus have

$$r_c = \frac{(\delta S_q)^2}{2\gamma q S \sin^2\theta} \tag{23}$$

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[7] For the sake of simplicity, we do not consider non-equilibrium effects, such as the dependence of E_{bs} upon dynamics in many biological adhesion systems.

This seems to become quite large if the contact angle is small. However, for the above approximations to hold, we must also observe that $\delta\theta$ must always remain smaller than θ. This entails $|\delta\theta| = \delta S/\gamma \sin\theta < \sin\theta$, or $\delta S < \gamma \sin^2\theta$. Thus $\tau < \delta S/4q$, and the critical radius fulfills

$$r_c < \frac{\delta S}{2qS} = \frac{\delta S}{S}\frac{\lambda}{4\pi} \tag{24}$$

which will never be even comparable to λ, since by assumption $\delta S \ll S$. In other words, a critical nucleus the size of which is determined by the inhomogeneity contribution to τ_{AB} will be much smaller than the length scale of the inhomogeneity itself. We can thus conclude that although inhomogeneities give rise to a quite well-defined contribution to the boundary tension, the size of the critical nucleus will not be dominated by these effects.

In conclusion, we have argued that although the analogy of nucleation in bulk systems on the one hand and in dewetting scenarios on the other hand suggests itself at first glance, it should be handled with great care. The main reason is that the long-range coupling of the substrate to the adjacent half space by virtue of the free liquid surface does in many cases not allow to assign an excess free energy to the boundary of a dry patch. Furthermore, there are usually not two coexisting film thicknesses into which the system may involve, which renders the analogy to bulk nucleation questionable. With due care, however, systems may be found which are completely analogous, such as the gravity dominated puddle. These allow the study of nucleation phenomena in a very imaginative way.

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