General stability criterion for wetting

Riccardo Rosso and Epifanio G. Virga
Dipartimento di Matematica, Istituto Nazionale di Fisica della Materia, Università di Pavia, Via Ferrata 1, 27100 Pavia, Italy
(Received 16 November 2002; published 11 July 2003)

We propose a general stability criterion for the wetting of solid substrates, both arbitrarily curved and inhomogeneous. In addition to the classical surface tension, the adhering drops can also exhibit a tension along the contact line where three phases meet, namely, the solid, the liquid, and the environment fluid. Moreover, we show how some stability issues currently debated in the specialized literature of disparate fields could profit from the application of this general criterion.

DOI: 10.1103/PhysRevE.68.012601 PACS number(s): 68.08.Bc

In its long history, the theory of capillarity has posed a wealth of mathematical problems [1], interest in which has possibly been revived by the emergence of wetting phenomena calling for a theoretical explanation. These phenomena include, but are not limited to, the effect of both material inhomogeneities and geometric microstructures of a solid substrate supporting a liquid drop (see, for example, [2,3]). They can also involve drops so small that a tension along the contact line plays a role in the free energy. The line tension of a drop can be viewed as Gibbs excess energy associated with the three phases in contact, namely, the solid, the liquid, and the environment fluid. As shown recently by Swain and Lipowsky [4], this tension alters the classical Young formula for the equilibrium condition along the contact line and also makes the contact angle depend on the differential properties of the substrate. For a given wetting liquid, the line tension is a constitutive property of the substrate and the surrounding environment; it notably depends on the temperature. Accurate measurements [5–7] have recently shown that away from the wetting transition the line tension ranges between 10^{-11} and 10^{-10} N and can be either positive or negative.

In this paper, we consider a general free-energy functional for a liquid drop in contact with a rigid substrate. The liquid is regarded as incompressible and is subject to a bulk potential; the substrate is taken to be an arbitrarily curved surface endowed with an adhesion potential varying from point to point, so as to represent both geometric microstructures and material inhomogeneities. Also a tension dependent on the position can act along the contact line. For this general energy functional we write the second variation in an intrinsic form, that is, with no resort to any specific representation of either the free surface of the drop or the substrate supporting it. When both the adhesion potential and the line tension are constant, the formula for the second variation becomes surprisingly simple. As is customary, the stability analysis of the equilibrium configurations for the drop is then reduced to an eigenvalue problem, which needs to be solved for specific equilibrium configurations. Here we mainly illuminate the role played by the contact line in a whole class of stability problems. That this is indeed a crucial role can easily be understood by the classical theorem in the theory of minimal surfaces, saying that the area functional is locally stable against perturbations confined to a sufficiently small region of the equilibrium surface [8]: all possible destabilizing causes thus arise from the border. A vast literature is devoted to these destabilizing effects; they are presumably hidden in most static dewetting mechanisms, but to our knowledge complete stability analyses have been confined either to flat, inhomogeneous substrates [9,10] or to special classes of curved substrates [11–13].

Below we first recall the mathematical preliminaries needed to make our general stability condition accessible to the nonspecialist. We then state our main conclusion, describing briefly the method employed to arrive at it. The paper closes with a list of open stability problems to which our analysis would be directly applicable.

Let $\mathcal{S}$ be a smooth orientable surface in the three-dimensional space with a border on a smooth closed curve $\mathcal{C}$ (see Fig. 1). An orientation is assigned to $\mathcal{S}$ by prescribing the unit normal $\boldsymbol{\nu}$; the outer conormal $\boldsymbol{\nu}_{\mathcal{S}}$ is defined on $\mathcal{C}$ as the outward unit vector tangent to $\mathcal{S}$ and orthogonal to $\mathcal{C}$; the border is further oriented so that its unit tangent is $\boldsymbol{t}:=\boldsymbol{\nu}_{\mathcal{S}}\times\boldsymbol{\nu}$. The trihedron $(\boldsymbol{t},\boldsymbol{\nu}_{\mathcal{S}},\boldsymbol{\nu})$ thus defined along $\mathcal{C}$ is called the Darboux trihedron (see [14], p. 261). Let s be the arclength of $\mathcal{C}$ oriented like $\boldsymbol{t}$. The Darboux trihedron rotates along $\mathcal{C}$ with *angular velocity* (see [15], p. 117) $\boldsymbol{\omega}=-\tau_g\boldsymbol{t}-\kappa_n\boldsymbol{\nu}_{\mathcal{S}}+\kappa_g\boldsymbol{\nu}$, where τ_g, κ_n, and κ_g, defined at every point of $\mathcal{C}$ by

$$\tau_g:=\frac{d\boldsymbol{\nu}}{ds}\cdot\boldsymbol{\nu}_{\mathcal{S}},\quad \kappa_n:=\frac{d\boldsymbol{t}}{ds}\cdot\boldsymbol{\nu},\quad \kappa_g:=\frac{d\boldsymbol{t}}{ds}\cdot\boldsymbol{\nu}_{\mathcal{S}},\tag{1}$$

are the geodesic torsion and the normal and geodesic curvatures of $\mathcal{C}$ relative to $\mathcal{S}$.

We consider now a liquid drop of a prescribed volume deposited on a curved, adhesive substrate. $\mathcal{B}$ is the region in space occupied by the drop and $\partial\mathcal{B}$ is its whole boundary,

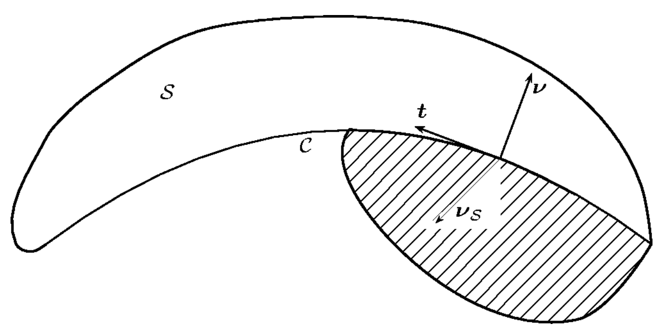

FIG. 1. A smooth surface $\mathcal{S}$ and its border $\mathcal{C}$: $(\boldsymbol{t},\boldsymbol{\nu}_{\mathcal{S}},\boldsymbol{\nu})$ is the Darboux trihedron.

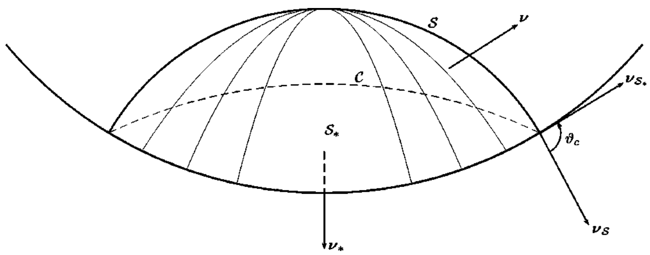

FIG. 2. Sketch of a drop deposited on a curved solid substrate. The boundary of the drop is composed of the *free* surface $\mathcal{S}$ and the *adhering* surface $\mathcal{S}_*$. The contact line $\mathcal{C}$ is the common border of $\mathcal{S}$ and $\mathcal{S}_*$.

which is composed of the *free* surface $\mathcal{S}$, where the drop is in contact with the environment fluid, and the *adhering* surface $\mathcal{S}_*$, where the drop is in contact with the substrate. The common border of $\mathcal{S}$ and $\mathcal{S}_*$ is the *contact line* $\mathcal{C}$ of the drop, where three distinct phases meet (see Fig. 2). The free-energy functional $\mathcal{F}$ of the drop is

$$\mathcal{F}[\mathcal{B}]=\int_{\mathcal{B}} f dv+\int_{\mathcal{S}}\gamma da+\int_{\mathcal{S}_*}(\gamma-w)da+\int_{\mathcal{C}}\tau ds, \quad (2)$$

where f is a bulk potential depending on the position in space, γ is the constant surface tension at the free surface, w is the adhesion potential of the substrate, and τ is the tension along the contact line. In Eq. (2), the interfacial energy on the substrate is conventionally written as $\gamma-w$, implying that $w>0$ for an adhesive substrate. Here both w and τ are taken as functions of the position on the substrate to describe constitutive material inhomogeneities. When both w and τ are constant, arbitrary geometric microstructures are still possible in the substrate.

The functional $\mathcal{F}$ is subject to the constraint on the volume of $\mathcal{B}$ and to the condition that $\mathcal{S}_*$ be part of the substrate. All admissible variations of $\mathcal{F}$ must preserve the drop volume and ensure that $\mathcal{S}_*$ *glides* on the substrate. In particular, a correct stability analysis relies on enforcing both these requirements up to the second order. Formally, we perturb the shape $\mathcal{B}$ of the drop by mapping every point p into

$$p_\varepsilon=p+\varepsilon\boldsymbol{u}+\varepsilon^2\boldsymbol{v}, \quad (3)$$

where ε is a perturbation parameter, and $\boldsymbol{u}$ and $\boldsymbol{v}$ are smooth vector fields describing the first- and second-order variations of $\mathcal{B}$, respectively. Both constraints are satisfied to the first order in ε, whenever $\boldsymbol{u}$ obeys

$$\int_{\mathcal{S}} u_\nu da=0, \quad (4)$$

$$\boldsymbol{u}\cdot\boldsymbol{\nu}_*=0 \quad \text{on } \mathcal{S}_*, \quad (5)$$

where $u_\nu := \boldsymbol{u}\cdot\boldsymbol{\nu}$ and $\boldsymbol{\nu}_*$ is the unit normal of $\mathcal{S}_*$ oriented outward to $\mathcal{B}$. Likewise, both constraints are satisfied to the second order in ε whenever $\boldsymbol{v}$ obeys

$$\int_{\mathcal{S}}(u_\nu \mathrm{div}_s\boldsymbol{u}-\boldsymbol{u}\cdot(\nabla_s\boldsymbol{u})^T\boldsymbol{\nu}+2\boldsymbol{v}\cdot\boldsymbol{\nu})da=0, \quad (6)$$

$$\boldsymbol{v}\cdot\boldsymbol{\nu}_*=-\frac{1}{2}\boldsymbol{u}\cdot(\nabla_s\boldsymbol{\nu}_*)\boldsymbol{u} \quad \text{on } \mathcal{S}_*, \quad (7)$$

where ∇_s denotes the surface gradient.

By requiring $\mathcal{F}$ to be stationary with respect to all first-order variations of $\mathcal{B}$, one arrives at the following equilibrium equations for the drop:

$$\gamma H+f=\Delta p \quad \text{on } \mathcal{S}, \quad (8)$$

$$\gamma\cos\vartheta_c+\gamma-w+\nabla_s\tau\cdot\boldsymbol{\nu}_{\mathcal{S}_*}-\tau\kappa_g^*=0 \quad \text{along } \mathcal{C}. \quad (9)$$

In Eq. (8), H is the total curvature of $\mathcal{S}$, and Δp is the Lagrange multiplier associated with the constraint on the volume and representing the pressure difference across the liquid-fluid interface. To make precise the sign convention adopted for H, we note that

$$\nabla_s\boldsymbol{\nu}=\sigma_1\boldsymbol{e}_1\otimes\boldsymbol{e}_1+\sigma_2\boldsymbol{e}_2\otimes\boldsymbol{e}_2, \quad (10)$$

where $\boldsymbol{e}_1$ and $\boldsymbol{e}_2$ are tangent unit vectors along the principal directions of $\mathcal{S}$ and σ_1,σ_2 are the corresponding principal curvatures. Here the total curvature of $\mathcal{S}$ is $H:=\mathrm{div}_s\boldsymbol{\nu}=\sigma_1+\sigma_2$, while the Gaussian curvature of $\mathcal{S}$, soon to be employed, is $K:=\sigma_1\sigma_2$. In Eq. (9), ϑ_c denotes the *contact angle*, that is, the angle made on the contact line $\mathcal{C}$ by the two conormal vectors $\boldsymbol{\nu}_{\mathcal{S}}$ and $\boldsymbol{\nu}_{\mathcal{S}_*}$, one relative to $\mathcal{S}$ and the other relative to $\mathcal{S}_*$; finally, κ_g^* is the geodesic curvature of $\mathcal{C}$ on $\mathcal{S}_*$. Since γ is constant, Eq. (8) also prescribes H to be a constant when $f=0$. Equation (8) is the classical Laplace equation, while Eq. (9), which in this form is due to Swain and Lipowsky [4], is a much newer generalization of the Young formula.

By Eqs. (4)–(9), the second variation $\delta^2\mathcal{F}$ of $\mathcal{F}$ on an equilibrium configuration of the drop can be given the following form:

$$\delta^2\mathcal{F}=\gamma\int_{\mathcal{S}}\{|\nabla_s u_\nu|^2+(2K-H^2+\partial_\nu f)u_\nu^2\}da-\gamma\int_{\mathcal{C}}\left(\frac{H^*}{\sin\vartheta_c}+\cot\vartheta_c H+\kappa_g\right)u_\nu^2 ds+\int_{\mathcal{C}}(\tau(u_s')^2-\{\tau[K^*+(\kappa_g^*)^2]+\nabla_s w\cdot\boldsymbol{\nu}_{\mathcal{S}_*}-(\nabla_s^2\tau)\boldsymbol{\nu}_{\mathcal{S}_*}\cdot\boldsymbol{\nu}_{\mathcal{S}_*}+\kappa_g^*\nabla_s\tau\cdot\boldsymbol{\nu}_{\mathcal{S}_*}\}u_s^2)ds. \quad (11)$$

In Eq. (11), u_ν and u_s are related on $\mathcal{C}$ through

$$u_\nu=\sin\vartheta_c u_s. \quad (12)$$

Moreover, $\partial_\nu f:=\nabla f\cdot\boldsymbol{\nu}$ is the normal derivative of f on $\mathcal{S}$, H^* and K^* are the total and Gaussian curvatures of $\mathcal{S}_*$, and a prime denotes differentiation with respect to the arclength s on $\mathcal{C}$. Clearly, when w is constant and τ vanishes on the substrate, the second line integral in Eq. (11) vanishes and $\delta^2\mathcal{F}$ acquires a much simpler form. In general, it is a remarkable feature of Eq. (11) that it depends only on the normal component of $\boldsymbol{u}$ on $\mathcal{S}$, while both $\boldsymbol{u}$ and $\boldsymbol{v}$ have nonvanishing tangential components.

A general stability criterion stems naturally from Eq. (11): an equilibrium configuration for the drop is stable whenever $\delta^2\mathcal{F}>0$ for all fields u_ν on $\mathcal{S}$ that satisfy Eq. (4). As is customary (see, for example, [16], p. 398), since $\delta^2\mathcal{F}$ is a quadratic functional, this criterion reduces to an eigenvalue problem. We abbreviate $\delta^2\mathcal{F}$ as γF with

$$F[u_\nu]:=\int_{\mathcal{S}}\{|\nabla_s u_\nu|^2+\alpha u_\nu^2\}da+\int_{\mathcal{C}}\{\xi(u_s')^2-\beta u_s^2\}ds, \tag{13}$$

where $\xi:=\tau/\gamma$ and α and β, which are immediately read off from Eq. (11), depend only on the given equilibrium shape of the drop. Seeking the fields u_ν that make F stationary subject to Eq. (4) and to

$$\int_{\mathcal{S}}u_\nu^2 da=1, \tag{14}$$

by resort to Eq. (12) we conclude that the equilibrium shape of the drop is stable whenever there are only positive values of μ for which the following equations in u_ν:

$$\Delta_s u_\nu+(\mu-\alpha)u_\nu+\lambda=0 \quad \text{on } \mathcal{S}, \tag{15}$$

$$\sin^2\vartheta_c \nabla_s u_\nu\cdot\boldsymbol{\nu}_{\mathcal{S}}-\sin\vartheta_c\left(\xi\left(\frac{u_\nu}{\sin\vartheta_c}\right)'\right)'-\beta u_\nu=0 \quad \text{along } \mathcal{C} \tag{16}$$

have a solution obeying both Eqs. (4) and (14). In Eq. (15), λ and μ are the Lagrange multipliers corresponding to the constraints in Eqs. (4) and (14), and Δ_s denotes the surface Laplacian.

Arriving at Eq. (11) is much more involved than one might expect from glancing at its harmless form. We show elsewhere [17] the details and the subtleties of this derivation; here we only record for the ease of the interested reader the basic tools that proved useful in several crucial points of the proof. We extensively employed the surface-divergence theorem (see, for example, [18], p. 87), which states that a smooth vector field $\boldsymbol{u}$ defined on the surface $\mathcal{S}$ satisfies the equation

$$\int_{\mathcal{S}}\text{div}_s\boldsymbol{u}\,da=\int_{\mathcal{S}}Hu_\nu da+\int_{\mathcal{C}}\boldsymbol{u}\cdot\boldsymbol{\nu}_{\mathcal{S}}ds. \tag{17}$$

Moreover, when $\mathcal{S}$ is sufficiently smooth the normal field $\boldsymbol{\nu}$ obeys [19]

$$\Delta_s\boldsymbol{\nu}=\nabla_s H+(2K-H^2)\boldsymbol{\nu}. \tag{18}$$

Finally, regarding $\mathcal{C}$ at the same time as a curve on $\mathcal{S}$ and as a curve on $\mathcal{S}_*$, the geodesic and normal curvatures and the geodesic torsions relative to the two surfaces can be related as follows [17]:

$$\kappa_g=\kappa_g^*\cos\vartheta_c+\kappa_n^*\sin\vartheta_c, \tag{19}$$

$$\kappa_n=\kappa_g^*\sin\vartheta_c-\kappa_n^*\cos\vartheta_c, \tag{20}$$

$$\vartheta_c'=\tau_g-\tau_g^*. \tag{21}$$

There are several problems arising in disparate fields that in our opinion would profit from the stability criterion shown in this paper. First, we briefly describe one such problem, for which our criterion already provides a definite answer. Then we quote a few more, for which the quest for a stability condition is still open in the specialized literature.

Line tension. Experiments with very small liquid drops, say, in the submicrometer range, have recently become common [5–7,21–23]. They support the theoretical predictions of an excess energy residing along the contact line (see, for example, [24,25], and [21], p. 174). Measurements of both positive and negative line tensions have been reported in the literature, fostering some theoretical debate. In particular, a qualitative argument has been put forward [26], which is not unanimously accepted [27], suggesting that the line tension must be positive for the stability of the drop. The possibility for the energy of selected fluctuations to be negative when the line tension is negative was similarly indicated in [28]. This conclusion essentially follows by arguing that for $\tau<0$ the line integral in Eq. (2) would make $\mathcal{F}$ unbounded from below for very wiggly lines $\mathcal{C}$ whose length prevails over the area of both surfaces $\mathcal{S}$ and $\mathcal{S}_*$. This is clearly conceivable only in the limit as the typical curvature $1/d$ of $\mathcal{C}$ tends to infinity. In this limit, however, the mesoscopic model where the drop's free energy is described by the functional $\mathcal{F}$ in Eq. (2) fails to be valid. Thus, when $\tau<0$, it becomes relevant to the stability of the drop to estimate within our model the minimum length d over all possible stable modes. This was achieved with the aid of our stability criterion for cylindrical liquid bridges lying on a flat substrate [17]. In particular, we studied the case where τ is constant, $f=0$, and $\gamma=w$, so that $\vartheta_c=\pi/2$ and the bridge is a semicylinder of radius R. We concluded that for $\tau=0$ all stable bridges have length $L<2\pi R$ and every bridge with length $L\geqslant 2\pi R$ is unstable: this is precisely the classical Rayleigh instability for a cylindrical liquid column, as when $\tau=0$ the energy of the semicylindrical bridge is precisely half the energy of the full column. When $\tau>0$, the line tension has a stabilizing effect, as the critical length L_c above which the bridges become unstable exceeds $2\pi R$. Precisely, when $\sqrt{\xi R}\ll L$, we estimated $L_c\approx 2\pi R+2\sqrt{\pi\xi R}$. Likewise, when $\tau<0$ the minimal length d over which the contact line $\mathcal{C}$ can be distorted, while leaving the second variation $\delta^2\mathcal{F}$ positive, is comparable to $\sqrt{|\xi|R}$. This is a mesoscopic length, intermediate between $|\xi|$ and R. Thus, when τ is negative also, semicylindrical bridges on a flat substrate are locally stable within our mesoscopic model.

Microscopic models like the one in [25] are more appropriate at shorter length scales. A kind of stability analysis within the model of [25] was performed in [29]: the functional whose minimum is interpreted as the line tension of the drop was found to be locally stable, irrespective of the sign of the line tension itself. To our knowledge, virtually all microscopic models, including the more refined ones [30,31] where the interface interactions are taken to be nonlocal, consider the drop as infinite and the contact line as straight.

A possible exception is the model proposed in [32], where the drop is a spherical segment and the contact line is a circle: there, however, the consequences of making both the surface and line tensions also depend on the curvatures of both the interface and the contact line are not explored. In our opinion, this avenue might lead to an improved variational model applicable down to length scales shorter than $\sqrt{|\xi|R}$, with $1/R$ generally a characteristic curvature of the drop.

Lotus effect. The leaves of some plants, an example of which is the lotus, exhibit a fine geometric microstructure that makes them repel virtually any liquid [33]. Several hypotheses have been put forward to explain this phenomenon [34,35]. A complete stability analysis would be eased by the criterion proposed here.

Fiber wetting. Coated fibers occur in many applications. Intuitively, the wetting mechanism that produces them should be affected by the instability of droplets trying to sit on the fiber. Recently, the need for a general stability criterion has clearly been felt in this field [36]. Indeed, Carroll [37] worked out an explicit metastability condition for barrel-like drops that has been further improved in some numerical explorations [12,13]. However, the outcomes of these studies cannot be applied to the more general mathematical models envisaged in [20]. It appears that these models fall within the range of validity of our criterion.

In conclusion, we arrived at a general stability criterion for the wetting of solid substrates: it applies to curved, inhomogeneous substrates bearing liquid drops with both surface and line tensions. We employed this criterion to decide the stability of liquid bridges with line tension. We also listed apparently disparate physical problems that could be solved by applying this general criterion. We plan to attack some of them in the near future.

It is our pleasure to acknowledge the valuable criticism of R. C. Ball and S. Luckhaus and the stimulating discussion with A. De Simone, J. Hinch, R. Lipowsky, and M. Warner at Castle Ringberg during the workshop Mathematical Aspects of Materials Science: Soft Matter, where our stability criterion was first presented. We are also grateful to G. Durand and G. Savaré for their comments and to the Italian GNFM (INdAM) for financial support to R.R.

[1] R. Finn, *Equilibrium Capillary Surfaces* (Springer, New York, 1986).
[2] P. Lenz and R. Lipowsky, Phys. Rev. Lett. **80**, 1920 (1998).
[3] R. Lipowsky, Interface Sci. **9**, 105 (2001).
[4] P.S. Swain and R. Lipowsky, Langmuir **14**, 6772 (1998).
[5] J.Y. Wang, S. Betelu, and B.M. Law, Phys. Rev. Lett. **83**, 3677 (1999).
[6] T. Pompe and S. Herminghaus, Phys. Rev. Lett. **85**, 1930 (2000).
[7] T. Pompe, Phys. Rev. Lett. **89**, 076102 (2002).
[8] J.L. Barbosa and M.P. do Carmo, Am. J. Math. **98**, 515 (1976).
[9] K. Sekimoto, R. Oguma, and K. Kawazaki, Ann. Phys. (N.Y.) **176**, 359 (1987).
[10] P. Lenz and R. Lipowsky, Eur. Phys. J. E **1**, 249 (2000).
[11] R.V. Roy and R.W. Schwartz, J. Fluid Mech. **391**, 293 (1999).
[12] G. McHale, N.A. Käb, M.I. Newton, and S.M. Rowan, J. Colloid Interface Sci. **186**, 453 (1997).
[13] G. McHale and M.I. Newton, Colloids Surf., A **206**, 79 (2002).
[14] M.P. do Carmo, *Differential Geometry of Curves and Surfaces* (Prentice-Hall, Englewood Cliffs, NJ, 1976).
[15] M. Kléman, *Points, Lines and Walls* (Wiley-Interscience, New York, 1983).
[16] R. Courant and D. Hilbert, *Methods of Mathematical Physics* (Wiley-Interscience, New York, 1953), Vol. 1.
[17] R. Rosso and E.G. Virga (unpublished).
[18] E.G. Virga, *Variational Theories for Liquid Crystals* (Chapman and Hall, London, 1994).
[19] R. Rosso and E.G. Virga, Proc. R. Soc. London, Ser. A **455**, 4145 (1999).
[20] C. Bieker and S. Dietrich, Physica A **252**, 85 (1998).
[21] *Applied Surface Thermodynamics*, edited by A.W. Neumann and J.K. Spelt (Marcel Dekker, New York, 1996).
[22] A. Marmur, Colloids Surf., A **136**, 81 (1998).
[23] A.I. Rusanov, Colloids Surf., A **156**, 315 (1999).
[24] P.G. de Gennes, Rev. Mod. Phys. **57**, 827 (1985).
[25] J.O. Indekeu, Physica A **183**, 439 (1992).
[26] D. Li, Colloids Surf., A **116**, 1 (1996).
[27] R. Lipowsky, P. Lenz, and P.S. Swain, Colloids Surf., A **161**, 3 (2000).
[28] A.S. Clarke, J. Chem. Phys. **96**, 9073 (1992).
[29] H. Dobbs, Physica A **271**, 36 (1999).
[30] T. Getta and S. Dietrich, Phys. Rev. E **57**, 655 (1998).
[31] C. Bauer and S. Dietrich, Eur. Phys. J. B **10**, 767 (1999).
[32] Y. Solomentsev and L.R. White, J. Colloid Interface Sci. **218**, 122 (1999).
[33] C. Neinhuis and E. Barthlott, Ann. Bot. (London) **79**, 667 (1997).
[34] S. Herminghaus, Europhys. Lett. **52**, 165 (2000).
[35] J. Bico, C. Tordeaux, and D. Quéré, Europhys. Lett. **55**, 214 (2001).
[36] C. Bauer and S. Dietrich, Phys. Rev. E **62**, 2428 (2000).
[37] B.J. Carroll, Langmuir **2**, 248 (1986).