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Roughness-induced filling

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We study adsorption of a fluid on a periodically corrugated substrate using the mean-field version of the effective Hamiltonian approach. We analyze the shape of the interface close to the wetting point of a planar substrate, and the free energy of the system as a function of temperature and amplitude of the corrugation for short-range and long-range interactions. We prove that the substrate roughness has no influence on the locus and order of the wetting transition, when the planar substrate of the same chemical composition as the corrugated one experiences critical wetting. For short-range interactions we observe the corrugation driven filling transition. We show analytically that a thin-thick first-order transition occurs when the corrugation amplitude of the substrate exceeds a critical value. The phase diagram of the adsorption on a sinusoidally corrugated substrate at the bulk liquid-gas coexistence is obtained.

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I. INTRODUCTION

In recent years the adsorption of a fluid on a structured substrate has been extensively studied experimentally and theoretically. While the wetting of a planar, homogenous substrate is well understood today [1–13], the wetting of a corrugated [14–37] or chemically heterogeneous substrate [38–47] is still a subject of wide interest and controversy. Apart from standard wetting transition, the liquid film adsorbed on a rough substrate can exhibit some new phenomena. One of them is an additional thin-thick transition, called filling transition [33,34]. It consists in filling up the hollows of the substrate with a liquid. Filling transition can be continuous, or first order, depending on a physical system. Another phenomenon discussed in the literature is the change of the location and order of the transition [27,31], it is the so called roughness-induced first-order wetting. In this paper we prove that (at the mean-field level) the corrugation-induced wetting transition cannot exist. We argue that if a planar substrate exhibits critical wetting, corrugated substrate made of the same substance undergoes critical wetting as well, without any change in the transition temperature. Although roughness of the substrate does not influence the wetting properties, it can induce the aforementioned filling transition. It is (if it exists) a first-order thin-thick transition, independent of whether wetting is a first-order or continuous transition.

The wetting phenomena are studied with the help of different methods such as Landau theory [9,11,27,30], the effective Hamiltonians [8,10,11,28,30,33–37], density functional theory [3,5,20], functional renormalization [6,8,10,11], computer simulations [12,13], and others. Here we adopt a simple, mean-field version of the effective Hamiltonian approach. When discussing without too far-reaching approximations that were made in Refs. [27,31], it does not reveal the aforementioned change of the transition. On the other hand, it is well known [11] that in the case of a planar substrate strong fluctuations can induce such change of the transition. This fluctuation influence can perhaps be amplified by the corrugation of the substrate, but at the mean-field level, the roughness of the substrate does not matter. Contrary to wetting, the filling transition is driven by the roughness of the substrate.

The organization of this paper is as follows. In Sec. II we introduce the system and give the simple, qualitative argument that the corrugation of the substrate has no influence on the location and the temperature of the transition. In Sec. III we recall the arguments for the existence of the corrugation driven first-order wetting. This phenomenon was predicted within the linearized version of the Hamiltonian approach [27,31]. We discuss this approximation and its applicability. With the help of the perturbative solution we show that the linear approximation is not justified in the regime where the corrugation-induced wetting was found. For the long-range interactions we show that within the framework of the linear approximation one observes, not only the first-order wetting, but additionally first-order dewetting followed by the continuous wetting. In Sec. IV we discuss nonperturbatively the system close to the wetting temperature of the planar substrate. Instead of solving a nonlinear equation for the shape of the interface, we minimize the effective Hamiltonian with respect to two parameters: the mean distance between substrate and interface, and the amplitude of the undulation of the film thickness. Similar analysis was made by Rascón, Parry, and Sartori [36]. We try to preserve the connection with the perturbative approach, and we obtain more information concerning the phase diagram. This minimization procedure is completely performed for short-range interactions. We discuss the free energy of the system as a function of the temperature and the amplitude of the corrugation, and show that when the system is close to the wetting critical point of the planar substrate, the roughness of the substrate changes it only insignificantly. Section V contains a proof of the nonexistence of the corrugation-induced wetting. Section VI contains our main result. In this section we analyze the filling transition. When the corrugation amplitude of the substrate exceeds the threshold value, first-order thin-thick transition occurs at temperature $T_f(A,q) < T_{w\pi}$ (A and q denote the corrugation amplitude and the wavelength of the substrate, respectively). Thus, while increasing temperature the system can exhibit a sequence of two transitions: the first-order filling, and next, the continuous wetting. We present the phase diagram of the system at the bulk liquid-gas coexistence. The adsorption on a sinusoidally corrugated substrate is determined by three parameters. First of them is the temperature, the remaining two have geometric origin: the roughness amplitude of the substrate, and the wave number of the substrate. We determine the coexistence line of the first-order filling transition, its critical point, and spinodal lines. We derive the mean-field values of critical exponents connected to the filling critical point. In Sec. VII we summarize our results.

II. WETTING OF THE CORRUGATED SUBSTRATE

When discussing the wetting transition of the corrugated substrate two important questions arise:

(1) Does the transition temperature remains unchanged as compared to the planar substrate of the same chemical composition?

(2) Does the wetting transition retains the same order?

A. The effective Hamiltonian approach

We consider the half space occupied by the fluid at bulk liquid-gas coexistence. The substrate is described by the function $z=b(\mathbf{R})$ where $\mathbf{R}$ denotes coordinates on the reference plane. The flat, planar substrate corresponds to the particular case $b(\mathbf{R})=0$. The simplest phenomenological approach deals with the effective interface Hamiltonian

$$\mathcal{H}[f]=\int d\mathbf{R}\left[\frac{\sigma}{2}(\nabla f)^2+\omega(l)\right], \tag{2.1}$$

where $f(\mathbf{R})$ and $l(\mathbf{R})=f(\mathbf{R})-b(\mathbf{R})$ are the interface position and the film thickness, respectively. σ is the surface tension of the free interface, and $\omega(l)$ is the effective interface potential, which is—by assumption—the same as for the planar substrate of the same chemical composition. The effective potential is chosen in such a way that it vanishes at infinity, therefore, Hamiltonian (2.1) describes the difference between the free energy of the actual configuration, and the free energy of planar interface situated infinitely far from the substrate. We call the effective potential first order or second order, depending on the order of the wetting transition at the planar substrate. First-order potential [Fig. 1(a)] has two minima, one at l_π—a finite distance of the flat interface from the planar substrate—and second one for the interface situated infinitely far from the substrate. If the temperature is lower than the wetting temperature $T_{w\pi}$ of the planar substrate, first minimum is deeper than the second one, and corresponds to negative value of $\omega(l)$; thus the equilibrium film thickness is equal to l_π. At $T_{w\pi}$ both minima have the same depth—the first-order wetting occurs at this temperature. On the contrary, the second-order potential [Fig. 1(b)] has only one minimum at l_π. The film thickness diverges continuously to infinity when temperature rises to $T_{w\pi}$. Corresponding value of the Hamiltonian $\mathcal{H}[l_\pi]$ is negative, and increases to zero when $T\nearrow T_{w\pi}$.

The equilibrium position of the interface $\overline{f}(\mathbf{R})$ minimizes the effective Hamiltonian (2.1) with respect to the appropriate boundary conditions, which are, at the moment, not specified. It fulfils the Euler-Lagrange equation

$$\sigma\Delta\overline{f}(\mathbf{R})=\omega'(\overline{l}(\mathbf{R})), \tag{2.2}$$

where the prime denotes the derivative of the potential ω with respect to its argument.

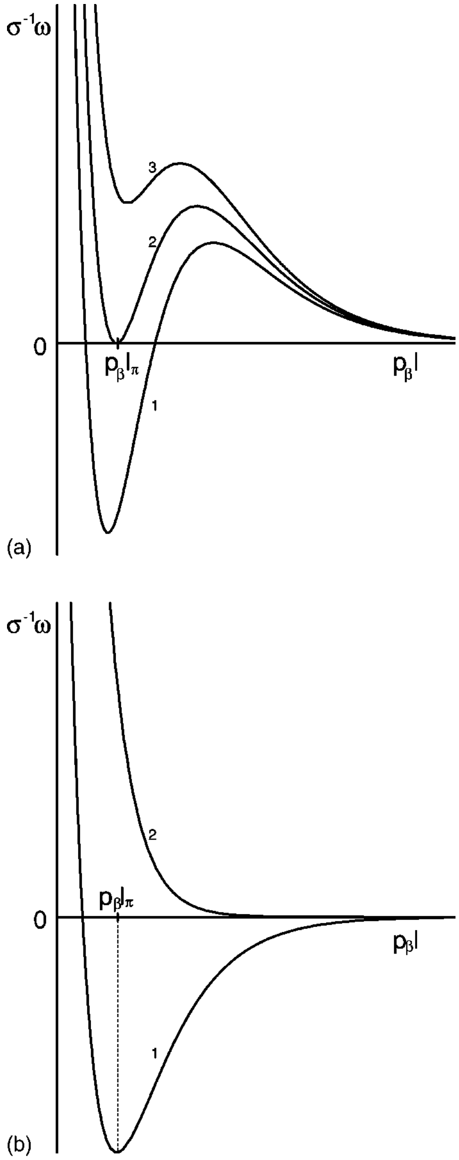

FIG. 1. (a) Plot of the first-order effective potential $\omega(l)$ for different values of temperature. Curves 1, 2, and 3 correspond to T lower, equal to, and greater than the wetting temperature of the planar substrate $T_{w\pi}$, respectively. l_π denotes the equilibrium film thickness on a planar substrate (in the figure only the value corresponding to curve 2 is marked). (b) Plot of the second-order effective potential $\omega(l)$ for different values of the temperature. Curve 1 corresponds to a temperature lower than $T_{w\pi}$, curve 2 corresponds to a temperature equal to or greater than $T_{w\pi}$. l_π denotes the equilibrium film thickness on a planar substrate.

The following qualitative analysis suggests the possibility of the nontrivial influence of the corrugation of the substrate on wetting transition. When the temperature is low, the second-order potential $\omega(l)$ has a deep and steep well with a global (negative) minimum at l_π—the mean-field film thickness on the planar substrate. For the potential contribution to the free energy it is advantageous that the film thickness preserves the value close to l_π; any deviation from this value considerably raises the free energy of the system. However, Hamiltonian (2.1) contains also (always non-negative) square-gradient contribution due to the undulation of the film thickness. For a liquid film of nearly constant thickness, the greater the corrugation of the substrate, the greater is the undulation of the interface, and the greater is the value of the square-gradient contribution. Thus, there is a competition between both contributions to the free energy. At high temperature, but smaller than $T_{w\pi}$, the potential well is broad and shallow. The negative potential contribution to the Hamiltonian is not so pronounced like at low temperatures. The small undulation of the interface is favorable, and the film thickness should be large everywhere. The increase of the free energy in the potential contribution to the Hamiltonian (2.1) resulting from the flattening of the interface is small, and can be compensated by decreasing the gradient contribution to the Hamiltonian. One can expect that the undulation of the interface induced by the corrugation of the substrate enforces the depinning transition. For large amplitude of the corrugation this gradient contribution could be perhaps large enough that at a specific temperature $T_w(A,q) < T_{w\pi}$ the free energy could have the same value as the free energy of the completely wet system. Thus, it would be a first-order transition occurring at $T_w(A,q) < T_{w\pi}$.

In the case of the first-order potential, the shift of the transition temperature is obvious [34]. At the wetting temperature of the planar substrate $T_{w\pi}$, both terms in Hamiltonian (2.1) are non-negative and the free energy of the finite interfacial profile is positive, whereas the free energy of the infinite configuration vanishes. At this temperature the infinite configuration is favorable. When the temperature is only a little bit lower than $T_{w\pi}$, it is so, as well. The effective interfacial potential $\omega(l)$ is negative in the vicinity of l_π, but its integral is still positive. The free energy of the finite solution vanishes at a specific temperature lower than $T_{w\pi}$. This indicates that in the case of the first-order potential the first-order wetting transition occurs at a temperature lower than the wetting temperature of the planar substrate, and the transition is a first-order one. The locus of the transition is determined both by the corrugation of the substrate and the effective potential $\omega(l)$.

The case of the second-order potential seems to be more complicated. Parry and collaborators [27,31] predicted that for small corrugation of the substrate, the wetting transition occurs exactly at $T_{w\pi}$ and remains critical. However, when the corrugation is strong enough, wetting occurs at a temperature lower then $T_{w\pi}$ and ceases to be critical. Instead of the continuous transition the authors report first-order transition. This phenomenon was called roughness-induced first-order wetting. Its existence was argued in different ways: with the help of the Landau theory, the effective Hamiltonian approach, and using arguments following from the functional renormalization and scalling theory. In the subsequent papers [35,36] the authors did not sustain this statement, or retract it. Instead, they wrote about another phenomenon—corrugation-induced first-order unbending—which is, in our terminology, identical to the filling transition. (Considering the phonetic conformity of terms *unbending* and *unbinding* we prefer the term *filling*). It is in agreement with the simple thermodynamical description of the rough surface [34], taking into consideration the competition between different surface contribution to the free energy. It is interesting to clarify this problem, and to investigate in detail how the interface behaves at a temperature close to the wetting point. We discuss here only the effective mean-field Hamiltonian approach. There is a simple counterexample, which shows that roughness-induced wetting cannot exist. Let us consider a flat interface f_0 situated at a large but finite distance from the substrate. The Hamiltonian (2.1) evaluated for this interface contains only potential contribution. For each value of the temperature less than $T_{w\pi}$, we can situate the interface so far that $\omega(l_0(\mathbf{R})) < 0$, what gives a negative value of $\mathcal{H}[f_0]$. At each temperature less then $T_{w\pi}$ the infinite configuration is not the configuration corresponding to the minimum of Hamiltonian (2.1); thus, it cannot be the equilibrium configuration. There is a whole spectrum of states f with a huge mean distance between the interface and the substrate, and with a small undulation of the interface, all of them have a negative value of $\mathcal{H}[f]$. The equilibrium interface has to be situated at a finite distance from the substrate. The wetting temperature cannot be shifted from $T_{w\pi}$ and wetting must be a continuous transition. This conclusion also remains true if we involve a more advanced Hamiltonian, for example, the "drum-head" model. All contributions containing derivatives of the interface vanish for planar interface, and only potential contribution survives. This argument, however, does not contradicts the existence of the roughness-induced thin-thick transition.

In this paper we discuss the periodically corrugated substrate described by the function

$$b(x) = A(1 - \cos qx). \tag{2.3}$$

A is called the corrugation amplitude of the substrate, q is the wave number of the substrate. The substrate is translationally invariant in y direction, what makes our problem quasi-one-dimensional. The half space with $z > b(x)$ is occupied by the fluid at bulk liquid-gas coexistence. We assume that the equilibrium interface has the same symmetry as the boundary and we restrict our consideration to one segment $[-a,a]$, with $a = \pi/q$. Thus, in Hamiltonian (2.1) integration can be restricted only to this segment

$$\mathcal{H}[f] = \int_{-a}^{a} dx \left[\frac{\sigma}{2} f_x^2 + \omega(l) \right]. \tag{2.4}$$

Our model has to be additionally supplemented by the boundary conditions

$$f_x(0) = f_x(a) = 0. \tag{2.5}$$

The Euler-Lagrange equation (2.2) now takes the form

$$\sigma \overline{f}_{xx}(x) = \omega'(\overline{l}(x)). \tag{2.6}$$

For $T < T_{w\pi}$, Eq. (2.6) has a solution situated at a finite distance from the substrate, and the solution situated at infinity. We are interested in competition (measured by the free energy) between them. At the beginning of our analysis we note a simple fact concerning the finite solution of Eq. (2.6). Integrating twice this equation with respect to x one obtains the inequality

$$f(a) - f(0) < \frac{a^2}{2\sigma} \max[\omega'(l)], \tag{2.7}$$

where $\max[\omega'(l)]$ denotes the maximal value of the derivative of $\omega'(l(x))$ over the segment $[0,a]$. For the second-order potential this maximal value decreases to zero when T grows to the wetting temperature of the planar substrate. This means that (independently of the competition) the finite solution flattens when $T \nearrow T_{w\pi}$, if the interface fulfills the condition $f(a) > f(0)$. This simple fact is important and we adduce it often in this paper.

B. Corrugation-induced first-order transition in the linear approximation: The shape of the interface

Predictions of the corrugation-induced first-order wetting were based on the linearized version of the theory. The Euler-Lagrange equation linearized around the equilibrium film thickness for the planar substrate l_π has the following form:

$$\left(\frac{d^2}{dx^2} - \frac{1}{\xi_{\parallel\pi}^2} \right) \overline{\delta l}(x) = -q^2 A \cos qx, \tag{2.8}$$

where $\overline{\delta l}(x) = \overline{l}(x) - l_\pi$ is the deviation of the local equilibrium value $\overline{l}(x)$ from its value l_π on the planar substrate. [Equation (2.6) can be linearized not necessarily around l_π but around another value l_0 (*a priori* arbitrary), see Appendix A.] The length $\xi_{\parallel\pi}$ defined by the equation

$$\omega''(l_\pi) = \frac{\sigma}{\xi_{\parallel\pi}^2} \tag{2.9}$$

is the parallel correlation length, also for the planar case. The linearization is justified by the fact that for the small corrgugation (i.e., for $qA \ll 1$) deviation $\overline{\delta l}(x)$ should be small, as well. However, this way of thinking restricts considerations only to the small corrugation, or low temperature, when such small deviation is energetically favorized. The solution of Eq. (2.8) satisfying boundary conditions $\overline{\delta l}_x(0) = \overline{\delta l}_x(a) = 0$ has the form

$$\overline{\delta l}(x) = \frac{(q\xi_{\parallel\pi})^2}{1 + (q\xi_{\parallel\pi})^2} A \cos qx. \tag{2.10}$$

The formal applicability of this solution is restricted to such range of the amplitude A and temperature that the film thickness $l_\pi + \delta l(x)$ is positive. This function has to be substituted to the Hamiltonian that, in linear approximation, takes the following form:

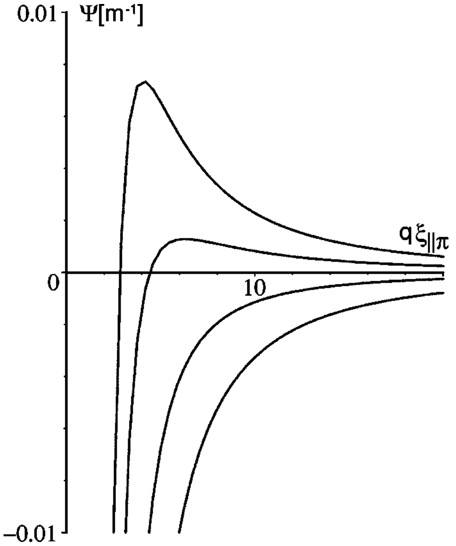

FIG. 2. Free energy $\Psi = 2p_\beta^2 F/\pi\sigma q$ for short-range interactions evaluated within the linear approximation as a function of the parallel correlation length on a planar substrate, $\xi_{\parallel\pi}$. This length is an increasing function of the temperature, and diverges at $T_{w\pi}$. Different plots correspond to the values of the corrugation amplitude of the substrate equal to (from bottom to top, respectively) $p_\beta A = 1.3, 1.38, 1.45, 1.5$. Last two curves satisfy the condition $p_\beta A > \sqrt{2}$. As the free energy of the infinitely thick layer with planar liquid-gas interface vanishes, these two curves exhibit the first-order wetting at their specific temperatures $T_w(A) < T_{w\pi}$.

$$\mathcal{H}[\delta f] = \int_{-a}^{a} dx \left\{ \frac{\sigma}{2} \left[(\delta f_x)^2 + \left(\frac{\delta l}{\xi_{\parallel\pi}} \right)^2 \right] + \omega(l_\pi) \right\}, \tag{2.11}$$

where $\delta f(x) = f(x) - (l_\pi + A)$. For the equilibrium solution one obtains

$$\overline{\delta f}(x) = -\frac{A}{1 + (q\xi_{\parallel\pi})^2} \cos qx. \tag{2.12}$$

This calculation is straightforward and gives the value of the free energy of the system

$$F = \frac{\sigma\pi q}{2p_\beta^2} \frac{(p_\beta A)^2}{1 + (q\xi_{\parallel\pi})^2} + \frac{2\pi}{q} \omega(l_\pi). \tag{2.13}$$

Here p_β denotes the inverse correlation length in the bulk liquid phase denoted by β. The above expression is valid both for the first- and for the second-order effective potential $\omega(l)$. Now we restrict our consideration to the second case. First contribution to the free-energy is positive, whereas the second one is negative. Thus, it can happen that for amplitude A large enough the free energy vanishes at a certain temperature $T_w(A,q)$ lower then the $T_{w\pi}$ (i.e., for finite values of l_π and $\xi_{\parallel\pi}$). As the free energy of the interface situated at infinity vanishes as well, it means that first-order wetting might occur at $T_w(A,q)$, provided the linear approximation is correct (see Fig. 2). However, one should be cautious as this result can violate the assumption that the corrugation is small, and in this case linearization of the theory is not justified.

We will investigate this problem separately for the short range, and for the long-range interactions. As a model of the short-range second-order interaction potential, we taken the interfacial potential of the form

$$\omega(l)=Wt\exp(-p_{\beta}l)+U\exp(-2p_{\beta}l), \tag{2.14}$$

where W and U are positive, temperature independent amplitudes of the attracting and repulsing potential, respectively, and $t=(T-T_{w\pi})/T_{w\pi}$ is the reduced temperature, which is negative below wetting of the planar substrate, and vanishes at $T_{w\pi}$. The free energy is equal to

$$F=\frac{\pi\sigma q}{2p_{\beta}^{2}}\left[\frac{(p_{\beta}A)^{2}}{1+(q\xi_{\parallel\pi})^{2}}-\frac{2}{(q\xi_{\parallel\pi})^{2}}\right]. \tag{2.15}$$

The first-order transition occurs at a temperature given implicitly (through the temperature dependence of $\xi_{\parallel\pi}$) by the equation

$$(q\xi_{\parallel\pi})^{2}=\frac{1}{\frac{1}{2}(p_{\beta}A)^{2}-1}, \tag{2.16}$$

if and only if the condition

$$(p_{\beta}A)^{2}>2, \tag{2.17}$$

is satisfied. The treshold of the first-order transition is defined by the amplitude $p_{\beta}A^{*}=\sqrt{2}$. In the following subsection we look for the solution of Eq. (2.6) perturbatively. We find the solution as a power series expansion in $p_{\beta}A$. When $p_{\beta}A>1$ what is the case of the first-order roughness-induced wetting, it is not allowed to neglect higher contributions and restrict considerations only to linearized theory. Thus, the first-order wetting induced by the corrugation occurs for such amplitude of the corrugation that linearization of the theory certainly is not justified.

As a model of the long-range second-order interactions we take into consideration the potential of the form

$$\omega(l)=\frac{Wt}{l^{r}}+\frac{U}{l^{s}}, \tag{2.18}$$

where r and s are natural numbers ($s>r$) while W, U, and t have the same meaning as in the previous case. The free-energy of the system is now equal to

$$F=\frac{\sigma\pi}{2q}\Gamma^{2}\left[\frac{\left(\frac{qA}{\Gamma}\right)^{2}}{1+(q\xi_{\parallel\pi})^{2}}-\frac{1}{(q\xi_{\parallel\pi})^{2s/(s+2)}}\right], \tag{2.19}$$

where

$$\Gamma^{2}=\frac{4(s-r)^{2/(s+2)}}{rs^{s/(s+2)}}\left(\frac{Uq^{s}}{\sigma}\right)^{2/(s+2)}. \tag{2.20}$$

The nonuniversality of the above expression is striking; the quantity Γ explicity depends on the surface tension σ of the free interface, and moreover, depends also on the amplitude U of the repulsing part of the effective potential $\omega(l)$. For small value of the nonuniversal amplitude qA/Γ, the free energy given by Eq. (2.19) is always negative, as long as the parallel correlation length is finite. Continuous wetting occurs at $T_{w\pi}$. If this amplitude is large enough, the first-order wetting occurs at a specific temperature $T_{1}(A,q)$. If the temperature grows, the first-order dewetting occurs at another specific temperature $T_{2}(A,q)>T_{1}(A,q)$. Above this temperature the substrate is once again partially wet and experiences the continuous wetting at $T_{w\pi}$ (see Fig. 3). At certain range of temperatures (T_{1},T_{2}) below $T_{w\pi}$ the wet state is stable, while for $T>T_{2}$ then substrate is only partially wet. We observe first-order dewetting at T_{2}, followed by the continuous wetting at $T_{w\pi}$. Depending on the value of the amplitude qA/Γ absolute values of minimum and maximum of the free-energy may differ about many orders of magnitude (see Fig. 3). Thus, for $T>T_{2}$ partially wet state or for $T_{1}<T<T_{2}$ completely wet state could be unstable with respect to fluctuations, provided the linear approximations were valid.

III. THE FILM THICKNESS FAR AWAY FROM THE CRITICAL WETTING OF THE PLANAR SUBSTRATE

In this section we solve Eq. (2.6) perturbatively. We discuss the short-range interactions and long-range interactions separately, although the method is the same for both cases.

A. Perturbative expansion

The general perturbative solution of Eq. (2.6) satisfying boundary conditions $l_{x}(0)=l_{x}(a)=0$ can be expressed as a power series expansion [48]

$$\overline{l}(x)=l_{\pi}+\sum_{i,j=1}^{\infty}B_{i,j}\cos^{j}qx\sin^{2j}qx. \tag{3.1}$$

Because $l(x)$ is even function of x, only even powers of $\sin qx$ give contribution to the film thickness $\overline{l}(x)$. The following polynomial expression:

$$\delta\overline{l}_{(n)}(x)=\sum_{i+2j=n}B_{i,j}\cos^{j}qx\sin^{2j}qx \tag{3.2}$$

will be called the nth order contribution to $\overline{l}(r)$. From Eq. (2.6) it follows that these contributions satisfy the hierarchy of equations

$$\left(\frac{d^{2}}{dx^{2}}-\frac{1}{\xi_{\parallel\pi}^{2}}\right)\delta\overline{l}_{(1)}(x)=-q^{2}A\cos qx, \tag{3.3}$$

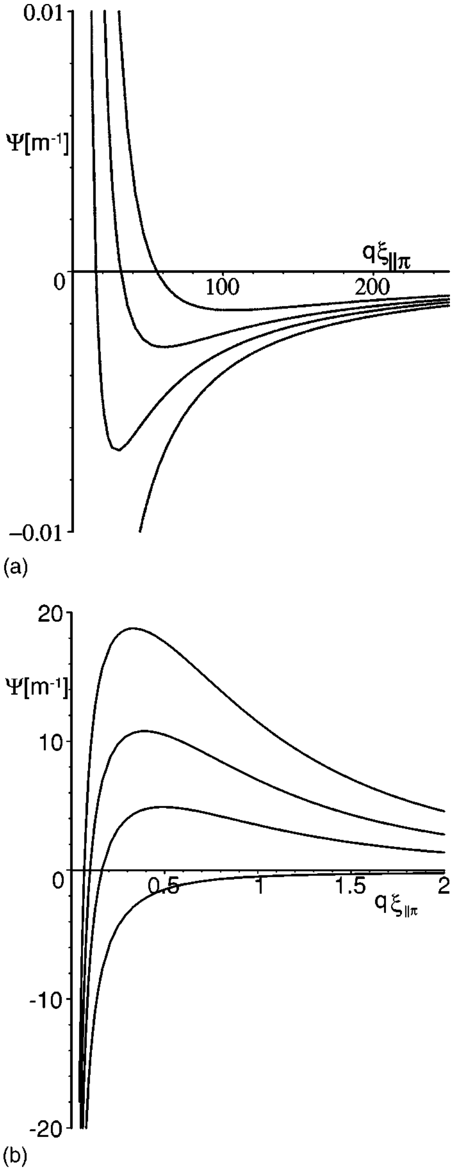

FIG. 3. Free energy $\Psi=2p_\beta^2F/\pi\sigma q$ for long-range interactions evaluated within the linear approximation as a function of the parallel correlation length on a planar substrate. Different plots correspond to the values of the corrugation amplitude of the substrate equal to (from bottom to top, respectively) $qA/\Gamma=1,3,4,5$. The first plot exhibits only the continuous wetting. Other curves exhibit more complicated behavior: the first-order wetting at a specific temperature $T_1(qA/\Gamma)$ (it is shown in the upper plot), and the first-order dewetting at another specific temperature $T_2(qA/\Gamma)$ greater than the previous one. Above $T_2(qA/\Gamma)$ the substrate remains only partially wet and experiences continuous wetting at $T_{w\pi}$, the wetting temperature of the planar substrate.

$$\left(\frac{d^2}{dx^2}-\frac{1}{\xi^2_{\parallel\pi}}\right)\delta\overline{l}_{(2)}(x)=\frac{1}{2\sigma}\omega^{(3)}(l_\pi)[\delta\overline{l}_{(1)}(x)]^2, \tag{3.4}$$

$$\left(\frac{d^2}{dx^2}-\frac{1}{\xi^2_{\parallel\pi}}\right)\delta\overline{l}_{(3)}(x)=\frac{1}{6\sigma}\omega^{(4)}(l_\pi)[\delta l_{(1)}(x)]^3+\frac{1}{\sigma}\omega^{(3)}\times(l_\pi)\delta\overline{l}_{(1)}(x)\delta\overline{l}_{(2)}(x), \tag{3.5}$$

$$\left(\frac{d^2}{dx^2}-\frac{1}{\xi^2_{\parallel\pi}}\right)\delta\overline{l}_{(4)}(x)=\frac{1}{24\sigma}\omega^{(5)}(l_\pi)(\delta\overline{l}_{(1)})^4+\frac{1}{2\sigma}\omega^{(4)}(l_\pi)\times[\delta\overline{l}_{(1)}(x)]^2\delta\overline{l}_{(2)}(x)+\frac{1}{2\sigma}\omega^{(3)}(l_\pi)\times\{[\delta\overline{l}_{(2)}(x)]^2+2\delta\overline{l}_{(3)}(x)\times\delta\overline{l}_{(1)}(x)\}\cdots. \tag{3.6}$$

This is a hierarchy of inhomogenous, linear, second-order differential equations; each inhomogenity is defined in terms of the solutions of previous equations. Thus, this hierarchy of equations can be easily solved step by step. First of them, Eq. (3.3), is the linearization of Eq. (2.6) around l_π. The solution of Eq. (3.3) has the form

$$\delta\overline{l}_{(1)}(x)=\frac{(q\xi_{\parallel\pi})^2}{1+(q\xi_{\parallel\pi})^2}A\cos qx. \tag{3.7}$$

It depends on the effective interfacial potential $\omega(l)$ only through the parallel correlation length $\xi_{\parallel\pi}$. The forms of the higher contributions $\delta\overline{l}_{(n)}(x)$ are explicitly ω dependent, and should be discussed separately for the short and for the long range of effective interactions.

B. Short-range interactions

Substituting to Eqs. (3.3)–(3.6) the solution in the form of the expansion given in Eq. (3.1), one obtains a system of linear equations for coefficient B_{ij}. First- and second-order contributions, i.e., $\delta\overline{l}_{(1)}$ and $\delta\overline{l}_{(2)}$ are given by the coefficients

$$B_{1,0}=\frac{(q\xi_{\parallel\pi})^2}{1+(q\xi_{\parallel\pi})^2}A, \tag{3.8}$$

$$B_{0,1}=3\frac{(q\xi_{\parallel\pi})^2}{1+4(q\xi_{\parallel\pi})^2}p_\beta B_{1,0}^2, \tag{3.9}$$

$$B_{2,0}=\frac{3}{2}\frac{1+2(q\xi_{\parallel\pi})^2}{1+4(q\xi_{\parallel\pi})^2}p_\beta B_{1,0}^2. \tag{3.10}$$

The expression for $\delta l_{(1)}(x)$ coincides with the solution [Eq. (2.10)] of the linear equation (2.8). It tends to A when temperature increases to $T_{w\pi}$. The second-order contribution $\delta\overline{l}_{(2)}$ tends to the constant value $\frac{3}{4}p_\beta A^2$ when temperature increases to $T_{w\pi}$. Third-order contribution $\delta\overline{l}_{(3)}$ has an amplitude proportional to $p_\beta^2A^3$ and vanishes at $T_{w\pi}$. Fourth-order contribution has an amplitude proportional to $p_\beta^3A^4$ and at $T_{w\pi}$ is equal to $-\frac{15}{64}p_\beta^3A^4$. This rule is general, $p_\beta\delta\overline{l}_{(n)}$ has an amplitude proportional to $(p_\beta A)^n$, vanishing at $T_{w\pi}$ for odd n, and nonvanishing for even n. Thus, the equilibrium film thickness is given asymptotically by the expression

$$\overline{l}(x)=\overline{l}_0+\frac{(q\xi_{\parallel\pi})^2}{1+(p_\beta\xi_{\parallel\pi})^2}A\cos qx+\delta\overline{f}(x), \tag{3.11}$$

where

$$\overline{l_0}=l_\pi+\tfrac{3}{4}p_\beta A^2-\tfrac{15}{64}p_\beta^3A^4+\cdots, \tag{3.12}$$

diverges logarithmically when temperature grows to $T_{w\pi}$. The term $\overline{\delta f}(x)$ vanishes at $T_{w\pi}$ [if follows from Eq. (2.7)], and the amplitude $(q\xi_{\parallel\pi})^2/[1+(p_\beta\xi_{\parallel\pi})^2]A$ of the film thickness undulation tends to the constant value A. The interface described by the finite solution moves continuously to infinity and becomes flat at $T_{w\pi}$, in agreement with Eq. (2.7).

From these considerations it follows that the linearization of Eq. (2.6) around l_π is not justified unless the amplitude $p_\beta A$ is less than one, or temperature is small. If this condition is not fulfilled, one must discuss the whole profile $\overline{l}(x)$ and not only $\delta\overline{l}_{(1)}(x)$. The prediction of the corrugation-induced first-order wetting was based on the linearized version of the theory. It turns out, that this transition occurs in the regime of amplitude $p_\beta A$ large enough that linearization is no longer justified. The whole perturbative expansion is needed, and the problem of its convergence arises. Instead of the perturbative solution of Eq. (2.6) we will employ in the following section an alternative procedure of investigation, which consists in direct minimization of the effective Hamiltonian.

C. Long-range interactions

The same analysis can be made for the long-range interactions described by the effective potential Eq. (2.18). For this case one obtains

$$B_{0,1}=\gamma_2\frac{(q\xi_{\parallel\pi})^2}{1+4(q\xi_{\parallel\pi})^2}\,\frac{qB_{1,0}^2}{(q\xi_{\parallel\pi})^{2/(s+2)}}, \tag{3.13}$$

$$B_{2,0}=\frac{1}{2}\,\gamma_2\frac{1+2(q\xi_{\parallel\pi})^2}{1+4(q\xi_{\parallel\pi})^2}\,\frac{qB_{1,0}^2}{(q\xi_{\parallel\pi})^{2/(s+2)}}, \tag{3.14}$$

with $B_{1,0}$ given by Eq. (3.8), and

$$\gamma_2=-\frac{r+s+3}{(s-r)^{1/(s+2)}}\left(\frac{\sigma}{sUq^s}\right)^{1/(s+2)}. \tag{3.15}$$

When T grows to $T_{w\pi}$, both $B_{0,1}$ and $B_{2,0}$ vanish. The interface moves to infinity and flattens just like for the previous case. Apart from the nonuniversality, there is one more difference; for short-range interactions l_0 differs from l_π, for long-range interactions it does not.

IV. INTERFACE CLOSE TO THE WETTING TRANSITION

From our previous considerations we know that the profile of the interface satisfying Euler-Lagrange equation at a temperature close to $T_{w\pi}$ is situated far away from the substrate (but still at a finite distance), and it is almost flat. When the temperature is close to $T_{w\pi}$, the interface flattens, and film thickness at the equilibrium can be described by the function

$$\overline{l}(x)=\overline{l_0}+\overline{B}\cos qx+\overline{\delta f}. \tag{4.1}$$

First parameter, $\overline{l_0}$ is divergent when T grows to $T_{w\pi}$, while $\overline{B}$ tends to A, and $\overline{\delta f}$ vanishes in this limit. In this regime it is possible to linearize Eq. (2.6) not around l_π—as we have done in the low-temperature regime—but rather around $\overline{l_0}+\overline{B}\cos qx$. Here $\overline{l_0}$ has the interpretation of the mean distance between interface and substrate, and $\overline{B}$ of the undulation amplitude of the film thickness. This new linearization procedure leads to a linear equation for $\overline{\delta f}$. However, this equation is not useful as the equilibrium values of $\overline{l_0}$ and $\overline{B}$ remain unknown.

We use an alternative approach, analogous to the one that was given by Rascón, Parry, and Sartori [36]. It is based on neglecting $\overline{\delta f}$ that is (in the vicinity of $T_{w\pi}$) much smaller than $\overline{l_0}$ and $\overline{B}$, substituting $l_0+B\cos qx$ instead of $l(x)$ into Hamiltonian (2.1), and minimizing the Hamiltonian with respect to l_0 and B. The neglected contribution contains higher terms of the Fourier series expansion that are relatively small in the vicinity of the wetting point of planar substrate [what follows from Eq. (2.7)]. (Here the absence of the bar sign denotes that this quantity has an arbitrary value, not necessarily an equilibrium one.) In this way the Hamiltonian in Eq. (2.1) ceases to be a functional of $f(x)$, but it becomes simply a function of both, l_0 and B,

$$\mathcal{H}(l_0,B)=\frac{1}{2}\sigma q\pi(B-A)^2+2\int_0^a dx\ \omega(l_0+B\cos qx). \tag{4.2}$$

Minimizing Hamiltonian (4.2) with respect to l_0 and B we obtain the equilibrium values $\overline{l_0}$ and $\overline{B}$ of these parameters. We discuss this procedure separately for short- and long-range interactions. In the following section we adopt this method also for the analysis of the filling transition.

A. Short-range interactions

In this subsection we discuss short-range interactions with the effective potential given by Eq. (2.14). We evaluate the potential contribution to the free energy expanding ω around l_0 and integrating this expansion step by step. In this way we obtain

$$\mathcal{H}(l_0,B)=\frac{1}{2}\sigma q\pi(B-A)^2+\frac{2\pi}{q}[tW\exp(-p_\beta l_0)\Phi(p_\beta B)+U\exp(-2p_\beta l_0)\Phi(2p_\beta B)], \tag{4.3}$$

where $\Phi(s)$ is a function defined as

$$\Phi(s)=\sum_{n=0}^{\infty}\frac{s^{2n}}{[(2n)!!]^2}, \tag{4.4}$$

where $s=p_\beta B$. This series expansion is bounded by the function $\cosh s$, and thus, it is convergent. It can be rewritten in terms of the hypergeometric function $F(\alpha,\gamma,s)$ [49] or modified Bessel function [50]

$$\Phi(s)=\exp(-s)F(\tfrac{1}{2},1,2s)=K_0(s). \tag{4.5}$$

Minimizing $\mathcal{H}(l_0,B)$ we have to solve the pair of equations (bars denote, as usual the equilibrium values)

$$\left(\frac{\partial\mathcal{H}}{\partial l_0}\right)\bigg|_B(\overline{l_0},\overline{B})=-\frac{2\pi p_\beta}{q}[tW\exp(-p_\beta\overline{l_0})K_0(p_\beta\overline{B})$$
$$+2U\exp(-2p_\beta\overline{l_0})K_0(2p_\beta\overline{B})]=0, \tag{4.6}$$

$$\left(\frac{\partial\mathcal{H}}{\partial B}\right)\bigg|_{l_0}(\overline{l_0},\overline{B})=\sigma q\pi(B-A)+\frac{2\pi p_\beta}{q}$$
$$\times[tW\exp(-p_\beta\overline{l_0})K_0'(p_\beta\overline{B})$$
$$+2U\exp(-2p_3\overline{l_0})K_0'(2p_\beta\overline{B})]=0. \tag{4.7}$$

(Prime denotes the derivative of the function with respect to its argument.) Equation (4.6) gives l_0 as the function of $p_\beta B$,

$$l_0(p_\beta B)=l_\pi+p_\beta^{-1}\ln\left(\frac{K_0(2p_\beta B)}{K_0(p_\beta B)}\right). \tag{4.8}$$

[Note that $K_0(s)$ is the increasing function of s, and in consequence expression in brackets in Eq. (4.8) is greater than one. Thus, $l_0(p_\beta B)>l_\pi$.] Expanding the right-hand side (rhs) of Eq. (4.8) (up to fourth-order terms in B) we obtain

$$l_0(p_\beta B)=l_\pi+\tfrac{3}{4}p_\beta B^2-\tfrac{15}{64}p_\beta^3B^4+\cdots. \tag{4.9}$$

For $T\nearrow T_{w\pi}$, $\overline{B}$ tends to A [it follows from Eq. (2.7)], and asymptotically

$$\overline{l_0}\equiv l_0(p_\beta\overline{B})\simeq l_\pi+\tfrac{3}{4}p_\beta A^2-\tfrac{15}{64}p_\beta^3A^4+\cdots, \tag{4.10}$$

what reproduces results of our perturbative approach, Eq. (3.12). We substitute the expression for $l_0(p_\beta B)$ given in Eq. (4.8) into Eq. (4.7). In this way we obtain an equation for the equilibrium value of $\overline{B}$,

$$p_\beta A=M(p_\beta B,q\xi_{\parallel\pi}), \tag{4.11}$$

where

$$M(p_\beta B,q\xi_{\parallel\pi})\equiv p_\beta\overline{B}+\frac{2}{(q\xi_{\parallel\pi})^2}\frac{K_0(p_\beta\overline{B})}{K_0(2p_\beta\overline{B})}$$
$$\times\left[K_0'(2p_\beta\overline{B})\frac{K_0(p_\beta\overline{B})}{K_0(2p_\beta\overline{B})}-K_0'(p_\beta\overline{B})\right]. \tag{4.12}$$

This is a transcendental equation that permits to find an equilibrium value of the corrugation amplitude of the interface $\overline{B}$ as a function of parameters A and q, which represent the geometry of the substrate p_β and $\xi_{\parallel\pi}$, which represent bulk and surface thermodynamics, respectively. The solution of Eq. (4.11) has to be next substituted to Eq. (4.8), to evaluate an equilibrium value of the mean distance $\overline{l_0}$. When temperature is close to $T_{w\pi}$, the factor $(p_\beta\xi_{\parallel\pi})^{-2}\ll 1$. In consequence, the second term on the rhs of Eq. (4.12) is very small as compared to $\overline{B}$. Thus, the equilibrium value of $\overline{B}$ is close to A, as we expected. The expression in square brackets in Eq. (4.12) is the nonmonotonic function of $\overline{B}$ (see Fig. 4), and the whole rhs of Eq. (4.12) is a nonmonotonic function provided $q\xi_{\parallel\pi}$ is enough small. There is a range of temperatures such that (depending on the value of the corrugation amplitude A, or wavenumber q) Eq. (4.11) can have more than one solution. This existence of more than one solutions turns out to be related to the filling transition. We will discuss this case in Sec. VI. Here we restrict our considerations to the case when $\xi_{\parallel\pi}$ is large enough (i.e., the temperature is close enough to $T_{w\pi}$) that Eq. (4.11) has a unique solution independently of the corrugation of the substrate.

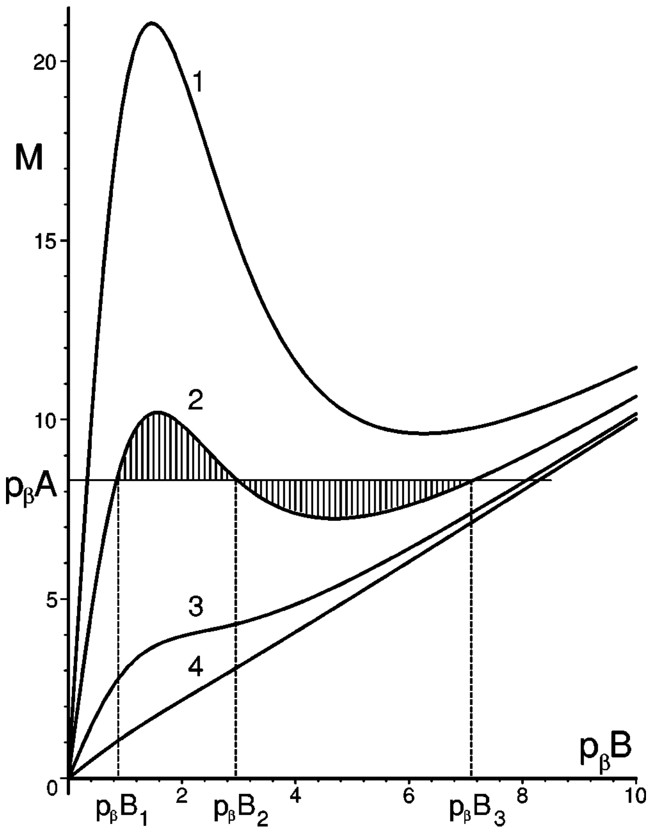

FIG. 4. Plot of $M(p_\beta B,q\xi_{\parallel\pi})$ [Eq. (4.12)] as a function of $p_\beta B$ for different values of $q\xi_{\parallel\pi}=0.1,0.15,0.3,1$ curves 1,2,3,4, respectively). For small values of $q\xi_{\parallel\pi}$ it is a nonmonotonic function. The equilibrium amplitude of the undulation of the interface $\overline{B}$ is defined by the intersection point of this plot with the straight, horizontal line, corresponding to the roughness amplitude $p_\beta A$ of the substrate. For the value of $p_\beta A$ corresponding to the horizontal line curve 1 leads to a small amplitude of the film thickness undulation. Curves 3 and 4 lead to large amplitudes of the film thickness undulation. Curve 2 corresponds to the first-order roughness-induced filling transition if the hatched surface areas shown in this figure are equal. Then the coexisting films have undulation amplitudes B_1 and B_3.

Looking for the coefficient $\overline{B}$ in the form

$$\overline{B}=\sum_{n=1}^{\infty}\alpha_n A^n, \tag{4.13}$$

we obtain

$$\overline{B}=A\,\frac{(q\xi_{\parallel\pi})^2}{1+(q\xi_{\parallel\pi})^2}\left[1+\frac{3}{8}\,\frac{(q\xi_{\parallel\pi})^4}{[1+(q\xi_{\parallel\pi})^2]^3}(p_3A)^2+\cdots\right]. \tag{4.14}$$

The first contribution to $\overline{B}$ coincides with the amplitude $B_{1,0}$ of the perturbative expansion Eq. (3.8). Higher contributions are negligible when temperature is close to $T_{w\pi}$. Using Eqs. (4.8) and (4.12) to evaluate Hamiltonian (2.6) we obtain the free energy of the system

$$F(T,A)=\frac{\pi\sigma q}{(q\xi_{\parallel\pi})^2p_\beta^2}\,\frac{K_0^2(p_\beta\overline{B})}{K_0(2p_\beta\overline{B})}\left[\frac{2}{(q\xi_{\parallel\pi})^2}\Lambda(p_\beta\overline{B})-1\right], \tag{4.15}$$

where $\overline{B}$ is a function of the amplitude A obtained from Eq. (4.11), and

$$\Lambda(s)=\frac{1}{K_0(2s)}\left[K_0'(2s)\,\frac{K_0(s)}{K_0(2s)}-K_0'(s)\right]^2. \tag{4.16}$$

Expanding Eqs. (4.14) and (4.15) up to terms quadratic in A one obtains the approximation of the free energy given in Eq. (2.15). First contribution in square bracket in Eq. (4.15) follows from the gradient term and is a positive quantity. Due to the factor $\xi_{\parallel\pi}^{-2}$ this contribution vanishes when T grows to $T_{w\pi}$. Close to $T_{w\pi}$ the whole expression in square bracket is negative. The interface situated at infinity has the free energy equal zero. Thus, the finite solution is the stable one. Moreover, the square bracket also has the prefactor $\xi_{\parallel\pi}^{-2}$. The free energy of the finite solution continuously grows to zero when temperature increases to $T_{w\pi}$. This proves that the corrugated system experiences the continuous wetting at $T_{w\pi}$, independently of the magnitude of A.

B. Long-range interactions

Similar analysis can be performed for the long-range interactions, Eq. (2.18). In this case

$$\mathcal{H}(l_0,B)=\frac{1}{2}\pi\sigma q(B-A)^2+\frac{2\pi}{q}\left[\frac{tW}{l_0^m}\Phi_r\left(\frac{B}{l_0}\right)+\frac{U}{l_0^m}\Phi_s\left(\frac{B}{l_0}\right)\right], \tag{4.17}$$

where

$$\Phi_k(\zeta)=\sum_{n=0}^{\infty}\frac{(k+2n-1)!}{(k-1)![(2n)!!]^2}\zeta^{2n}, \tag{4.18}$$

where $\zeta=B/l_0$. For $\zeta<1$, the power series (4.18) is bounded by the function $\frac{1}{2}[(1+\zeta)^{1/k}+(1-\zeta)^{1/k}]$. It can be rewritten as the Barnes' extended hypergeometric function

$$\Phi_k(\zeta)=F\left(\left(\frac{1}{2}(k+1),\frac{1}{2}k\right),1,\zeta^2\right)\quad(k=r,s). \tag{4.19}$$

Close to $T_{w\pi}$ the fraction $\overline{B}/\overline{l}_0$ is much less than one, and the expansion (4.18) is convergent. Equation (4.6) gives the following expression for l_0 as a function of B:

$$l_0(p_\beta B)=l_\pi\left(\frac{\Gamma_s\left(\frac{B}{l_0}\right)}{\Gamma_r\left(\frac{B}{l_0}\right)}\right)^{1/(s-r)}, \tag{4.20}$$

where

$$\Gamma_k(\zeta)=\Phi_k(\zeta)+\frac{1}{k}\zeta\Phi_k'(\zeta)\quad(k=r,s). \tag{4.21}$$

[Equation (4.20) when solving together with Eq. (4.7) with respect to A corresponds to Eq. (10) in the paper of Rascón, Parry, and Sartori [36].] Equation (4.20) is a transcendental equation for l_0 as a function of B. We can solve this equation perturbatively, substituting

$$l_0=l_\pi\left(\sum_{n=0}^{\infty}\alpha_nB^n\right). \tag{4.22}$$

Solving Eq. (4.20) up to second order in B we obtain

$$l_0=l_\pi\left(1+\frac{r+s+3}{4}\left(\frac{B}{l_\pi}\right)^2+\cdots\right). \tag{4.23}$$

This is a behavior quite different than for short-range interactions. In the former case l_π has an additive correction while in the present case it has a multiplicative correction. When T grows to $T_{w\pi}$ this factor tends to unity. Thus, asymptotically $\overline{l}_0$ is equal to l_π, which is in agreement with results of the perturbative approach.

For long-range interactions instead of Eq. (4.7) we obtain

$$A=\overline{B}+\frac{2}{\sigma q^2}\left[\frac{Wt}{\overline{l}_0^{r+1}}\Phi_r'\left(\frac{\overline{B}}{\overline{l}_0}\right)+\frac{U}{\overline{l}_0^{s+1}}\Phi_s'\left(\frac{\overline{B}}{\overline{l}_0}\right)\right]. \tag{4.24}$$

Unfortunately, in this case $\overline{l}_0$ and $\overline{B}$ are not separated like for short-range interactions: Eq. (4.24) depends not only on $\overline{l}_0$, but also on $\overline{B}/\overline{l}_0$. This makes the calculations (although possible) more cumbersome. Instead of solving Eqs. (4.6) and (4.7) and expressing the free energy only by the equilibrium value of $\overline{B}$ we perform in the following section a rigorous analysis, valid for both kind of interactions.

V. THE PROOF OF THE NONEXISTENCE OF THE ROUGHNESS-INDUCED WETTING

Computational difficulties for the long-range interactions are not the only reason for the search of an exact proof of the nonexistence of the roughness-induced first-order wetting. In

Hamiltonian (4.2) we have omitted all contributions containing $\delta\bar{f}$ and its derivatives. In the potential contribution to the Hamiltonian, this neglected term is indeed small as compared to the leading term $\omega(\bar{l}_0+\bar{B}\cos qx)$. It is not obvious that terms containing derivative $\delta\bar{f}_x$ are also negligible. The expressions $(\delta\bar{f}_x)^2$ and $2(B-A)\bar{f}_x$ are compared to $(\bar{B}-A)^2$; all of them can vanish in the similar way. In order to elucidate this problem we proceed in another way. We substitute the equilibrium solution $\bar{f}$ of the Euler-Lagrange equation (2.6) into Hamiltonian (2.4), and integrate gradient term by parts. In this way we obtain

$$\mathcal{H}[\bar{f}]=2\int_0^a dx[-\omega'(\bar{l})\bar{f}+\omega(\bar{l})]. \tag{5.1}$$

We have to compare the value of $\mathcal{H}[\bar{f}]$ to zero—the value of the free energy of the planar interface situated at infinity. Negative value of $\mathcal{H}[\bar{f}]$ means that the substrate is only partially wet, positive value of $\mathcal{H}[\bar{f}]$ means that it is completely wet. The first term of the integrand in Eq. (5.1) is positive. Integrating Eq. (2.6) from 0 to a, due to the boundary conditions $\bar{l}_x(0)=\bar{l}_x(a)=0$ we obtain

$$\int_0^a dx\,\omega'(\bar{l})=0. \tag{5.2}$$

Equation (5.2) generalizes to the case of the corrugated substrate the condition

$$\omega'(l_\pi)=0, \tag{5.3}$$

which defines the equilibrium film thickness l_π on the planar substrate. The position of the equilibrium interface $\bar{f}(x)$ can be rewritten as

$$\bar{f}(x)=\bar{l}_0-\frac{A}{1+(p_\beta\xi_{\parallel\pi})^2}\cos qx+\delta\bar{f}(x)=\bar{l}_0+\Delta\bar{f}(x), \tag{5.4}$$

where (as we know from our previous considerations) $\bar{l}_0$ is divergent when $T\nearrow T_{\parallel\pi}$. (It need not be equal to l_π, and for short-range interactions it is not), while $\delta\bar{f}(x)$, and $\Delta\bar{f}(x)$ vanish as temperature increases to the wetting temperature of the planar substrate. With the help of Eq. (5.2) we can rewrite Eq. (5.1) as

$$\mathcal{H}[\bar{f}]=2\int_0^a dx[-\omega'(\bar{l})\Delta\bar{f}+\omega(\bar{l})]. \tag{5.5}$$

When interactions are short range, all contributions to $\omega(\bar{l})$ and $\omega'(\bar{l})$ asymptotically decay like $\xi_{\parallel\pi}^{-2}$ when temperature grows to $T_{w\pi}$. However, $\omega'(\bar{l})$ is multiplied by $\Delta\bar{f}$, which itself is decaying like $\xi_{\parallel\pi}^{-2}$, as well. [See also Eq. (4.15).] In consequence, the square-gradient contribution to the free energy is asymptotically negligible as compared to the potential contribution; the negative contribution to the free energy dominates over the positive one. In the case of long-range interactions, the asymptotical difference between the square-gradient and potential contributions to the free energy is even more pronounced; $\omega(\bar{l})$ decays like l_π^{-s}, while $\omega'(\bar{l})$ decays faster, like $l_\pi^{-(s+1)}$.

This proof can be immediately generalized for the case of an arbitrary, periodically corrugated substrate.

VI. FILLING TRANSITION

The filling transition occurs when the coexistence between thin and thick films adsorbed on the substrate is possible. We discuss this transition in the case of short-range interactions. We consider the Hamiltonian

$$\mathcal{H}(l_0(p_\beta B),p_\beta B,q\xi_{\parallel\pi})=\frac{\pi\sigma q}{p_\beta^2}\left[\frac{12}{2}(p_\beta B-p_\beta A)^2-\frac{1}{(q\xi_{\parallel\pi})^2}\frac{K_0^2(p_\beta B)}{K_0(2p_\beta B)}\right], \tag{6.1}$$

$[l_0(p_\beta B)$ is given by Eq. (4.8)] as a function of B. For $B=\bar{B}$ it determines the free energy of the system. For fixed $q\xi_{\parallel\pi}$ Hamiltonian (6.1) has—independently of the value of A—a single minimum provided $q\xi_{\parallel\pi}\geqslant 0.492$. For $q\xi_{\parallel\pi}<0.492$ there exists such range of amplitude A that this minimum splits into two minima separated by a maximum. In this case Eq. (4.11) has two or three solutions. The filling transition emerges from the competition between these solutions. We denote them by $\bar{B}_i$ $(i=1,2,3)$, and by F_i the free energies corresponding to them. The film with the undulation amplitude $\bar{B}_2$ always has a free energy greater than the others. In fact, it corresponds to the maximum of $\mathcal{H}(l_0(p_\beta B),p_\beta B,q\xi_{\parallel\pi})$, whereas $\bar{B}_1$, and $\bar{B}_3$ correspond to the local minima of Hamiltonian (6.1). The derivative of the Hamiltonian (6.1) with respect to B fulfills the equation

$$\frac{d}{dB}\mathcal{H}(l_0(p_\beta B),p_\beta B,q\xi_{\parallel\pi})=\left(\frac{\partial\mathcal{H}}{\partial B}\right)\bigg|_{l_0}(l_0(p_\beta B),p_\beta B,q\xi_{\parallel\pi}), \tag{6.2}$$

due to Eq. (4.6). The function defined by Eq. (6.2) is equal to $M(p_\beta B,q\xi_{\parallel\pi})-A$ [see Eq. (4.11)]. The free energies F_1 and F_3 are related through the equation

$$F_3=F_1+\int_{\bar{B}_1}^{\bar{B}_3}dB\,\frac{d}{dB}\mathcal{H}(l_0(p_\beta B),p_\beta B,q\xi_{\parallel\pi}). \tag{6.3}$$

This equation implies that there (for fixed $q\xi_{\parallel\pi}$) the first-order filling transition occurs when

$$\int_{\bar{B}_1}^{\bar{B}_3}dB\,\frac{d}{dB}\mathcal{H}(l_0(p_\beta B),p_\beta B,q\xi_{\parallel\pi})=0 \tag{6.4}$$

The above equation indicates that the locus of the transition is determined by the Maxwell's construction. Equation (6.4) points out that the surface areas between the plot of the function $M(p_\beta B,q\xi_{\parallel\pi})$ and the horizontal line $p_\beta A$ shown on

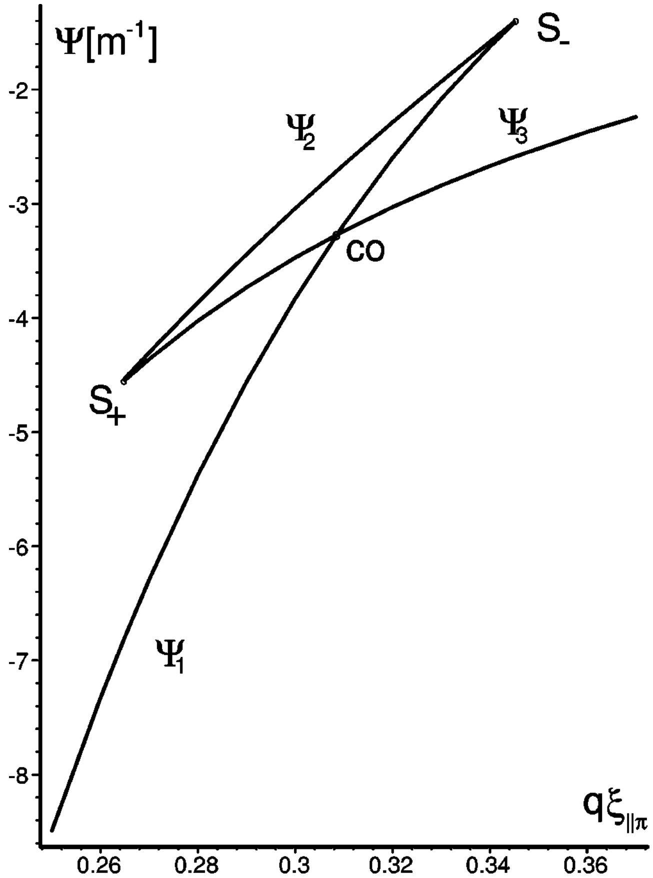

FIG. 5. The free energy $\Psi = p_\beta^2 F/\pi\sigma q$ of the films adsorbed on the sinusoidally corrugated substrate with $p_\beta A = 4$. Free energies Ψ_1, Ψ_2, and Ψ_3 correspond to undulation amplitudes of the film thickness B_1, B_2, and B_3, respectively. CO denotes the filling transition point. For $q\xi_{\|\pi} > (q\xi_{\|\pi})_{\mathrm{CO}}$ the equilibrium film has an undulation amplitude B_3. Similarily, for $q\xi_{\|\pi} < (q\xi_{\|\pi})_{\mathrm{CO}}$ the equilibrium film has an undulation amplitude B_1. The metastable liquid films may also exist. The line CO-S_- corresponds to the metastable thin film, while the line CO-S_+ corresponds to the metastable thick film. $S_\pm$ denotes the lower or upper spinodal point, respectively.

Fig. 4 are equal. Figure 5 presents the plot of the free energies F_1, F_2, and F_3 as functions of $q\xi_{\|\pi}$. It displays the characteristic behavior of the chemical potential of the van der Waals fluid at two-phase coexistence. The value $q\xi_{\|\pi}$ equal to 0.492 determines the critical point of the coexistence line between the profile with large undulation and profile with small undulation of the film thickness. The critical filling temperature depends on the wave number q of the substrate; it grows when decreasing q. Figure 6 presents the adsorption diagram of the system expressed in variables $(q\xi_{\|\pi})^{-1}$ and A. The wetting transition is described by the straight vertical bold line $(q\xi_{\|\pi})^{-1} = 0$, $A \geqslant 0$. The point denoted as CF is the critical filling point. There are three lines terminating at this point. The middle line is the first-order filling transition line. Lines situated below and above it are spinodals. They are border lines of metastable states: thick metastable layer between the transition line and the lower spinodal, and thin metastable layer between the transition line and the upper spinodal.

The critical point has coordinates

$$(q\xi_{\|\pi})_{\mathrm{CF}} = 0.492, \quad p_\beta A_{\mathrm{CF}} = 2.469. \tag{6.5}$$

All numerical values are quoted with the error less than 0.001. The critical amplitude A_{CF} is the treshold value of the corrugation amplitude A; the corrugation-induced filling transition occurs when $A \geqslant A_{\mathrm{CF}}$. When $q\xi_{\|\pi} < (q\xi_{\|\pi})_{\mathrm{CF}}$, the function $M(p_\beta B, q\xi_{\|\pi})$ (for fixed $q\xi_{\|\pi}$) displays a maximum and a minimum separated by an inflection point $p_\beta B_i = 1.203$. At the critical point maximum and minimum vanish, they shrink into the inflection point. In the critical region the coexistence line is described by the function (for details see Appendix B)

$$p_\beta A = p_\beta B_i + \frac{f(p_\beta B_i)}{(q\xi_{\|\pi})^2} = 1.203 + \frac{0.306}{(q\xi_{\|\pi})^2}. \tag{6.6}$$

When $q\xi_{\|\pi}$ has a value fixed close to the critical one, and $p_\beta B$ has a value close to $p_\beta B_i$ the function $M(p_\beta B, q\xi_{\|\pi})$ can be approximated by the polynomial of third order in $\Delta B = B - B_i$. Thus, the asymptotic behavior of different quantities can be easily found. The undulation amplitudes $B_{3,1}$ at thin-thick coexistence satisfy in the vicinity of the filling-critical point following mean-field power laws:

$$\Delta \overline{B}_{3,1} \sim \begin{cases} \left(\dfrac{T_{\mathrm{CF}} - T}{T_{\mathrm{CF}}}\right)^{1/2} & \text{for } q = \text{const}, \\ \left(\dfrac{q_{\mathrm{CF}} - q}{q_{\mathrm{CF}}}\right)^{1/2} & \text{for } T = \text{const}. \end{cases} \tag{6.7}$$

The coexistence line is described by the linear asymptotic law

$$\frac{A_{\mathrm{CF}} - A}{A_{\mathrm{CF}}} \sim \begin{cases} \dfrac{T_{\mathrm{CF}} - T}{T_{\mathrm{CF}}} & \text{for } q = \text{const}, \\ \dfrac{q_{\mathrm{CF}} - q}{q_{\mathrm{CF}}} & \text{for } T = \text{const}. \end{cases} \tag{6.8}$$

Thus, Eq. (6.7) also reads as

$$\Delta \overline{B}_{3,1} \sim \left(\frac{A - A_{\mathrm{CF}}}{A_{\mathrm{CF}}}\right)^{1/2}. \tag{6.9}$$

For spinodals the asymptotic behavior is determined by the following power law:

$$A_- - A_+ \sim \begin{cases} \left(\dfrac{T_{\mathrm{CF}} - T}{T_{\mathrm{CF}}}\right)^{3/2} & \text{for } q = \text{const}, \\ \left(\dfrac{q_{\mathrm{CF}} - q}{q_{\mathrm{CF}}}\right)^{3/2} & \text{for } T = \text{const}. \end{cases} \tag{6.10}$$

The singular part of the free energy of the system at thin-thick coexistence $[q\xi_{\|\pi} < (q\xi_{\|\pi})_{\mathrm{CF}}]$ behaves as

$$F_{\mathrm{sing}} \sim [(q\xi_{\|\pi})^2_{\mathrm{CF}} - (q\xi_{\|\pi})^2]^2, \tag{6.11}$$

which leads to

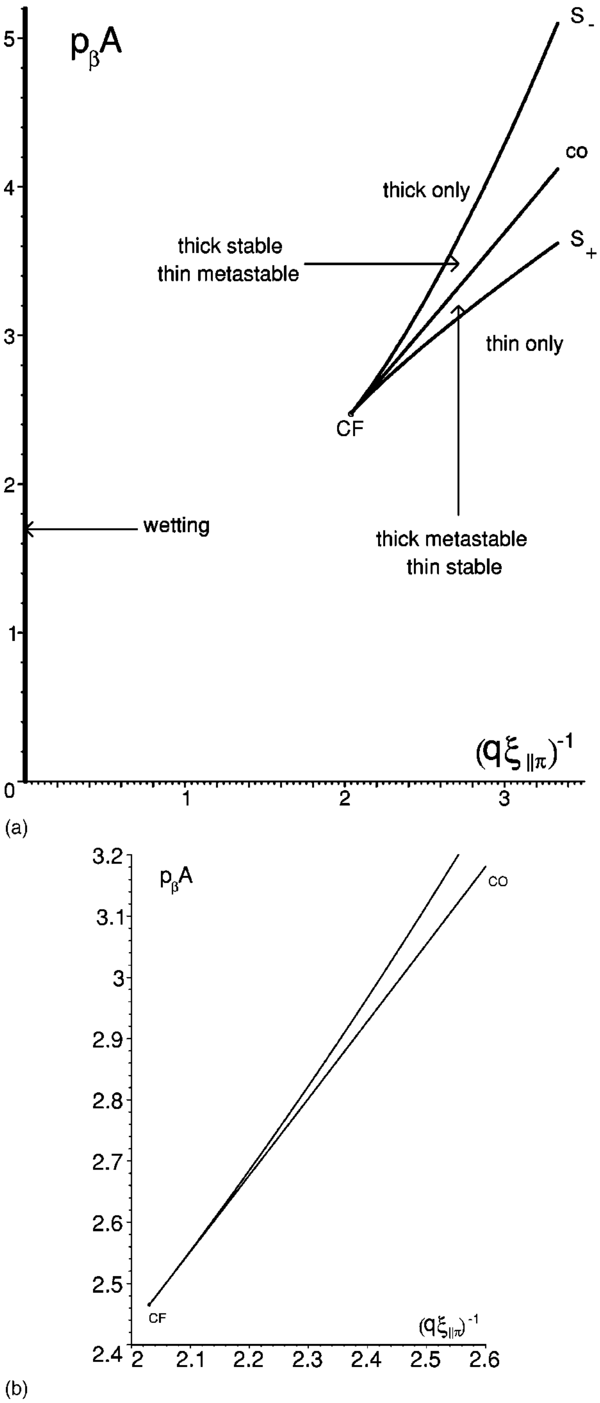

FIG. 6. (a) The adsorption diagram of the sinusoidally corrugated substrate at the bulk liquid-gas coexistence. Bold vertical line $(q\xi_{\|\pi})^{-1}=0$, $A\geqslant 0$ is the location of the wetting transition. The first-order filling transition line is denoted here by CO, the critical filling point by CF, $S_\pm$ are the corresponding spinodals. Above the coexistence line the equilibrium liquid film is thick, but below the upper spinodal S_- a thin metastable layer may exist. Below the coexistence line the thin layer is stable, but above the lower spinodal S_+ a metastable, thick liquid film may exist. (b) The coexistence line in the critical region. CO denotes the coexistence line obtained numerically (CF is the critical filling point). The curve above the coexistence line is defined by Eq. (6.6). In the vicinity of the critical point both lines coincide.

$$F_{\text{sing}}\sim\begin{cases}\left(\dfrac{T_{\text{CF}}-T}{T_{\text{CF}}}\right)^2 & \text{for } q=\text{const},\\[2ex] \left(\dfrac{q_{\text{CF}}-q}{q_{\text{CF}}}\right)^2 & \text{for } T=\text{const}.\end{cases}\tag{6.12}$$

The nonanalyticity of the free energy in filling critical region is described by the following power law:

$$F_{\text{sing}}\sim\left(\frac{T_{\text{CF}}-T}{T_{\text{CF}}}\right)^{2-\alpha_F}.\tag{6.13}$$

This means that the exponent α_F defined by Eq. (6.13) is equal to zero. It follows from these considerations that there are three significant variables: temperature T (it enters the analysis through the parallel correlation length $\xi_{\|\pi}$ on the planar substrate), the corrugation amplitude A, and the wave number q. Albeit the last one is only a prefactor accompanying $\xi_{\|\pi}$, it plays an important role. The filling criticality can be achieved not only upon increasing the temperature but also upon increasing the wave number. For constant temperature and corrugation amplitude A, the greater q is, the greater is the corrugation parameter qA, the system is closer to the filling critical point. The change of the wave number q causes the vertical shift of interfaces. For smaller q (i.e., for larger size of the segment) the system is closer to wetting criticality, and the distance between interface and the substrate is larger. Figure 7 presents an example of coexisting films at fixed T.

VII. SUMMARY

In some physical systems the adsorption of a liquid on a two-dimensional corrugated substrate is not restricted to a simple (first order or continuous) wetting. One of the possible scenarios is the sequence of two transitions: first-order thin-thick transition followed by the continuous wetting. Such behavior was found experimentally when investigating the wetting of hexane (or, more generally, alkanes) by water [51]. In this system, thin-thick transition that precedes wetting is driven by the competition between short-range and long-range effective interactions. Similar sequence can happen in a quite different system with simpler interactions (only short-range or only long-range interactions), when the substrate is not planar, but exhibits large enough corrugation. In this paper we have studied the influence of the roughness of the substrate on the adsorption phenomena. Unfortunately, the experimental results in this field today are not rich enough and they do not allow to compare theoretical results with experimental data.

Our first conclusion is that the roughness of the substrate has no influence on the order of the mean-field wetting transition. If planar substrate experiences continuous wetting at temperature $T_{w\pi}$, the sinusoidally corrugated substrate also experiences continuous wetting transition at the same temperature. The form of the Hamiltonian used in this work in principe is restricted only to small roughness of the substrate. We have used this form not only for its simplicity. It was

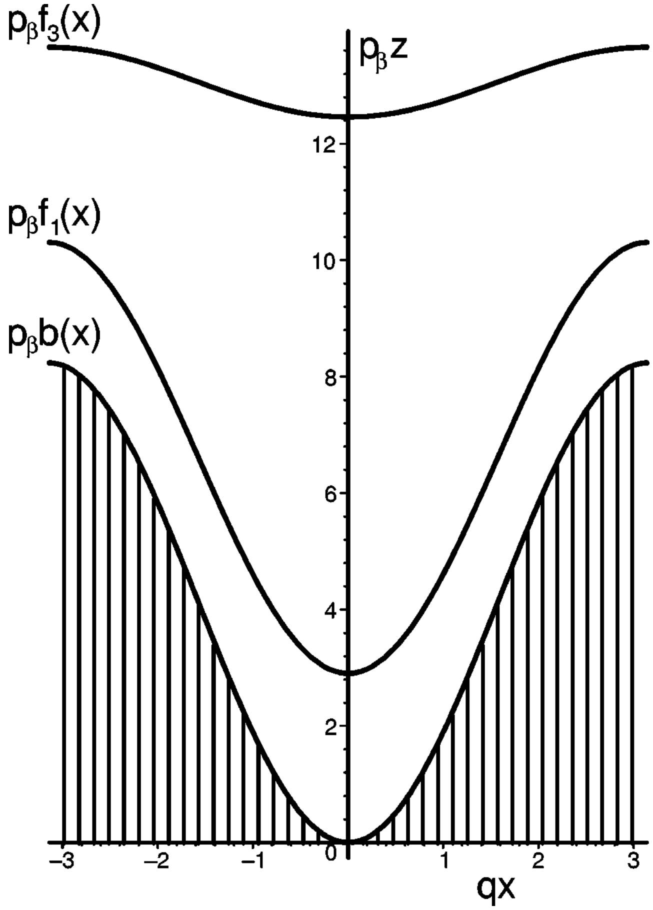

FIG. 7. The example of coexisting films on sinusoidally corrugated substrate ($p_\beta A=4.112$). The hatched area represents the substrate; $f_1(x)$ and $f_2(x)$ are liquid-gas interfaces of coexisting films.

used in the paper [31], where the corrugation-induced wetting was predicted with its help. The simplification of this model is not so important, because the roughness of the substrate depends on both A and q. Even with a huge value of the amplitude A, the corrugation can be small if the wave number q is small enough. Instead of Hamiltonian (2.1) we could use the more complicated "drum-head" model

$$\mathcal{H}[f]=\int dx\left[\frac{\sigma}{2}(\sqrt{1+f_x^2}-1)+\omega(l)(\sqrt{1+b_x^2})\right], \tag{7.1}$$

where the factor $\sqrt{1+b_x^2}$ reflects enlargement of the area of the substrate due to its corrugation. It could even be supplemented by the curvature contributions. Independently of possible generalizations, our general argument against the existence of the corrugation-induced wetting given in Sec. II remains valid. For each value of the temperature less than $T_{w\pi}$ there always exists a flat, planar interface, such that the effective Hamiltonian (7.1) is negative, i.e., the interface situated at infinity does not correspond to the global minimum of Hamiltonian. In Sec. IV and Sec. V we have described in details how the substrate becomes wet. We have used a simple method of the minimization of the effective Hamiltonian. It permits to avoid looking for solutions of the nonlinear equation, which is usually a difficult problem. This simple, direct minimization makes it possible to describe the asymptotic properties of the system close to the wetting point, and describe the filling transition. An analogous method was used in Ref. [36]. Our analysis is more detailed; we have established the connection of this method to the perturbative approach, and we have extracted more information (i.e., coexistence line, spinodals, critical exponents, and nonexistence of the roughness driven first-order wetting transition). Rigorous approach excludes the possibility of the existence of the mean-field roughness driven first-order wetting. Beyond the mean-field theory there is an open problem concerning the influence of the fluctuations on the wetting transition. This problem is worth of an effort because the fluctuations of the liquid-gas interface situated over a flat substrate can change the temperature and the order of wetting transition. One can expect that roughness of the substrate comes into a play through the fluctuations of the interface [11].

Although the corrugation of the substrate does not influence the wetting transition, it induces another phenomenon, namely, the corrugation-induced filling transition. For the wedge geometry the filling transition occurs for each value of the opening angle of the wedge, and has the same order as the wetting transition (at least for a very open wedge). When the substrate has a saw shape, the filling (first-order) transition occurs only when wetting is a first-order transition, and the corrugation amplitude of the substrate is large enough. On the contrary, on the sinusoidally corrugated substrate filling transition occurs even when wetting is continuous. It is always a first-order transition and ceases to exist when the roughness amplitude of the substrate has a value less than the critical one. Our main result is the adsorption diagram at the liquid-gas bulk coexistence. We have found the analytical expressions determining the coexistence line, and spinodals in the vicinity of the filling critical point, and we have calculated mean-field values of the critical exponents.

The filling transition (in both cases, i.e., in the wedge and on the sinusoidally corrugated substrate) was predicted when using purely thermodynamical arguments [24,33,34]. If the balance between different surface contributions to the free energy is taken into account, one can expect that the phase transition between an empty well and a well partially filled with a liquid appears. Thermodynamic prediction of the filling temperature in a wedge is exact but the order of the transition is not determined at this level. On the contrary, in the case of the sinusoidal substrate, thermodynamics predicts the order of the transition well, but other predictions are not confirmed by the mean-field theory. In particular, thermodynamics states the existence of the filling transition independently of the corrugation amplitude. It is an open question why in some cases thermodynamics and mean-field theory are in good agreement and in some cases they are not.

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APPENDIX A

In this appendix we prove that the linearization of Eq. (2.6) is an unambiguous procedure. In Sec. II B we have linearized Eq. (2.6) around the equilibrium value of the film thickness l_π at the planar substrate. It is possible to linearize this equation around another value l_0 (*a priori* arbitrary). The linearized equation can be written in the following form:

$$(1-s^2)L''(s)-sL'(s)+sA=\frac{\omega'(l_0)}{\sigma q^2}+\frac{\omega''(l_0)}{\sigma q^2}L(s). \tag{A1}$$

where $l(x)=l_0+L(s)$ and $s=\cos qx$. The solution of Eq. (A1) can be formally written in the form of a power series expansion

$$L(s)=\sum_{k=0}^{\infty} l_k s^k, \tag{A2}$$

with coefficients satisfying equations

$$l_2=\frac{\omega'(l_0)}{\sigma q^2}, \tag{A3}$$

$$l_3=\frac{1}{6}\left[\left(1+\frac{\omega''(l_0)}{\sigma q^2}\right)l_1-A\right], \tag{A4}$$

and for $k>3$

$$l_{k+2}=\frac{1}{(k+2)(k+1)}\left(k^2+\frac{\omega''(l_0)}{\sigma q^2}\right)l_k, \tag{A5}$$

where l_0 and l_1 are arbitrary numbers. First, we look for the solution that is a polynomial of the nth order. In this case the coefficient l_{n+2} vanishes (l_{n+1} vanishes as well) and we get the following equation defining l_0:

$$\omega''(l_0)=-n^2\sigma q^2. \tag{A6}$$

For a fixed temperature the existence of the solutions of the above equation depends on the wavelength of the substrate q. The smaller the value of q the greater must be n, such that there exists at least one solution. Note that for a large value of the amplitude A of the roughness of the substrate the wave number q has to be small in order to fulfill the condition $qA \ll 1$. When temperature increases, the solutions corresponding to large n cease to exist, and close to $T_{w\pi}$ only the basic solution described Sec. II B survives. The condition $l_{n+1}=0$ leads to the conclusion that (except l_1) all odd coefficients have to vanish; otherwise $\omega'(l_0)=0$, which, however, for second-order interaction potential is in contradiction with a negative value of $\omega''(l_0)$. There is an additional restriction imposed on each solution, namely, that $l(x)$ must be positive for each x. Here, we list the solutions corresponding to $n=2,4,6$:

$$l_2(x)=l_{0_2}-\frac{A}{3}\cos qx+\frac{\omega'(l_{0_2})}{\sigma q^2}\cos^2 qx, \tag{A7}$$

$$l_4(x)=l_{0_4}-\frac{A}{15}\cos qx+\frac{\omega'(l_{0_4})}{\sigma q^2}(\cos^2 qx-\cos^4 qx), \tag{A8}$$

$$l_6(x)=l_{0_6}-\frac{A}{35}\cos qx+\frac{\omega'(l_{0_6})}{\sigma q^2}\left(\cos^2 qx-\tfrac{8}{3}\cos^3 qx+\tfrac{16}{9}\cos^6 qx\right). \tag{A9}$$

In the above expressions l_{0_n} denotes solution of the Eq. (A6) corresponding to the appropriate value of n. The free energy corresponding to $l_2(x)$ is equal to

$$F_2=\frac{\pi\sigma q}{2}\left[\frac{4}{3}A^2+\frac{1}{2}\left(\frac{\omega'(l_{0_2})}{\sigma q^2}\right)^2\right]+\frac{2\pi}{q}\omega(l_{0_2}). \tag{A10}$$

Let us recall the free energy of the basic solution from Sec. II A. It is equal to

$$F_1=\frac{\pi\sigma q}{2}\frac{A^2}{1+(q\xi_{\parallel\pi})^2}+\frac{2\pi}{q}\omega(l_\pi). \tag{A11}$$

The first contribution to F_2 is evidently greater than the first contribution to F_1. As l_π corresponds to the absolute minimum of the effective potential ω, the same holds for the second contributions to both expressions. In consequence, $F_1<F_2$ what makes the solution $l_2(x)$ uninteresting. Nevertheless, we take this solution into consideration for a moment. In Eq. (A10) we replace l_{0_2} by an arbitrary value l_0, and evaluate derivatives of F_2 with respect to l_0,

$$\frac{dF_2}{dl_0}=\frac{2\pi}{q}\omega'(l_0)\left[1+\frac{\omega''(l_0)}{4\sigma q^2}\right]. \tag{A12}$$

This derivative vanishes when $\omega''(l_0)=-4\sigma q^2$ what defines l_{0_2} [Eq. (A6) in the case of $n=2$; moreover, note that $\omega'(l_{0_2})\neq 0$]. In general, Eq. (A10) has two solutions $l_{0_2}^{(1)}$ and $l_{0_2}^{(2)}$ ($l_{0_2}^{(1)}<l_{0_2}^{(2)}$). The second derivative of F_2 evaluated at l_{0_2} is equal to

$$\left.\frac{d^2F_2}{dl_0^2}\right|_{\omega''(l_{0_2})=-4\sigma q^2}=\frac{\pi}{2\sigma q^3}\omega'''(l_{0_2})\omega'(l_{0_2}). \tag{A13}$$

For both values of l_{0_2} the first derivative $\omega'(l_{0_2})$ is positive, whereas the third derivative $\omega'''(l_{0_2})$ is negative for $l_{0_2}^{(1)}$ and positive for $l_{0_2}^{(2)}$ value of l_{0_2}. Thus, function $F_2(l_0)$ has the maximum at $l_{0_2}^{(1)}$, and minimum at $l_{0_2}^{(2)}$. The free energy of the above described additional solutions contains the contribution dependent on the amplitude of the corrugation of the substrate. This contribution has the form $(\pi\sigma q/2)[n^2(qA)^2/(n^2-1)]$, which is always greater than the corresponding contribution to the free energy for the basic solution, which is equal to $(\pi\sigma q/2)\{(qA)^2/[1+(q\xi_\parallel)^2]\}$. The total free energy of these solutions is greater than the free energy of the solution linearized around l_π.

Moreover—and this is the crucial point—these solutions do not correspond to the minima of the Hamiltonian (2.11). The second variation of the Hamiltonian is given by the following expression:

$$\delta^2\mathcal{H}=\int_{-a}^{a} dx[\sigma(\Delta l_x)^2+\omega''(l_0)(\Delta l)^2]. \tag{A14}$$

For the variation Δl of the film thickness of the form $\Delta l = c\cos qx$, it is equal to

$$\delta^2\mathcal{H}=\pi\sigma q c^2\left[1+\frac{\omega''(l_0)}{\sigma' q^2}\right]. \tag{A15}$$

The necessary condition of the minimum of the Hamiltonian is

$$\frac{\omega''(l_0)}{\sigma q^2}>-1, \tag{A16}$$

which is violated in the case of these polynomial solutions. When the condition (A6) is not fulfilled for any value of n, Eqs. (A2)–(A5) define an infinite power series expansion. It is convergent for arbitrary values of l_0 and l_1, what follows from Raabe's criterion. Even in the case $l_0=l_\pi$ there is a family of convergent expansions corresponding to the free choice of l_1 (for $l_0=l_\pi$ the expansion exhibits only odd powers of s). On the other hand the formal power series expansion corresponding to $L''(s)$ is not convergent, and (except the aforementioned uninteresting polynomial solutions) Eq. (A2) does not define new solutions of Eq. (2.8). Thus, the linearization of Eq. (2.6) around l_π is a unique choice, and there are no other solutions of the linearized theory than Eq. (2.10).

APPENDIX B

In this appendix we present the details of calculations leading to the determination of the critical properties of the system. We rewrite the function $M(p_\beta B, q\xi_{\|\pi})$ defined by Eq. (4.12) in the following form:

$$M(p_\beta B,q\xi_{\|\pi})=p_\beta B+\frac{1}{(q\xi_{\|\pi})^2}f(p_\beta B). \tag{B1}$$

Both functions M and f have the same inflection point $p_\beta B_i = 1.203$. In this point

$$f''(p_\beta B_i)=M''(p_\beta B_i,q\xi_{\|\pi})=0, \tag{B2}$$

In the filling critical point additionally

$$M'(p_\beta B_i,(q\xi_{\|\pi})_{\mathrm{CF}})=0. \tag{B3}$$

(Prime denotes the derivative with respect to $p_\beta B_i$.) Equation (B3) can be rewritten in the following form

$$f'(p_\beta B_i)=-(q\xi_{\|\pi})^2_{\mathrm{CF}}. \tag{B4}$$

We expand M around $p_\beta B_i$ up to third-order terms in $\Delta B = B - B_i$ in the vicinity of the critical filling point. With the help of Eqs. (B2) and (B4) we obtain

$$\begin{aligned}M(p_\beta B,q\xi_{\|\pi})=p_\beta B_i+p_\beta\Delta B+\frac{1}{(q\xi_{\|\pi})^2}&\\ \times[f(p_\beta B_i)-(q\xi_{\|\pi})^2_{\mathrm{CF}}\Delta p_\beta B&\\ +\tfrac{1}{6}f'''(p_\beta B_i)(p_\beta\Delta B)^3].&\end{aligned} \tag{B5}$$

For the equilibrium solution, $M(p_\beta\overline{B},q\xi_{\|\pi})=p_\beta A$, and moreover the Maxwell's construction has to be fulfilled. For a given value of A we chose $q\xi_{\|\pi}$ in such way, that Eq. (6.6) is fulfilled. Thus

$$\frac{\Delta B}{(q\xi_{\|\pi})^2}[\tfrac{1}{6}f'''(p_\beta B_i)(p_\beta\Delta B)^2+(q\xi_{\|\pi})^2-(q\xi_{\|\pi})^2_{\mathrm{CF}}]=0. \tag{B6}$$

Equation (B6) has three solutions; $\Delta B=0$ and

$$\Delta B_\pm=\pm\sqrt{\frac{6}{f'''(p_\beta B_i)}[(q\xi_{\|\pi})^2_{\mathrm{CF}}-(q\xi_{\|\pi})^2]}. \tag{B7}$$

We will show that the choice given in Eq. (6.6) satisfies the Maxwell's construction within our approximation

$$\begin{aligned}\int_{B_-}^{B_+}dB[M(p_\beta B,q\xi_{\|\pi})-p_\beta A]=\Bigg\{\left[1-\frac{(q\xi_{\|\pi})^2_{\mathrm{CF}}}{(q\xi_{\|\pi})^2}\right]\frac{(p_\beta\Delta B)^2}{2p_\beta}&\\ -\frac{f'''(p_\beta B_i)}{24p_3}(p_\beta\Delta B)^4\Bigg\}\Bigg|_{B_-}^{B_+}.&\end{aligned} \tag{B8}$$

As for both solutions $(\Delta B)^2$ has the same value, the above integral vanishes, and $\overline{B}_1=B_-$, $\overline{B}_2=B_i$, $\overline{B}_3=B_+$. Equation (6.6) states that asymptotically along the coexistence line A is the quadratic function of $(q\xi_{\|\pi})^{-1}$. Moreover, we have shown that close to the critical filling point the Maxwell's construction is equivalent to such choice of $q\xi_{\|\pi}$ (for a fixed A) that the straight horizontal line $p_\beta A$ in Fig. 4 intersects the plot of the function M at the inflection point. Numerically obtained phase diagram (Fig. 6) displays rather the linear dependence of A on $(q\xi_{\|\pi})^{-1}$. It does not contradicts the asymptotics obtained analytically. In fact, in the critical region one observes the crossover between line and quadratic behavior of the coexistence line [see Fig. 6(b)].

In a similar manner we determine the location of spinodals in the vicinity of the critical filling point. They are defined by the condition

$$M'(p_\beta B,q\xi_{\|\pi})=0. \tag{B9}$$

We denote the solutions of Eq. (B9) by $B_{s\pm}$; the plus sign corresponds to greater value of the amplitude B. We expand Eq. (B9) around $p_\beta B_i$ up to square terms in $\Delta B_s = B_s - B_i$. In this way we obtain

$$\tfrac{1}{2}f'''(p_\beta B_i)(p_\beta\Delta B_s)^2=(q\xi_{\|\pi})^2_{\mathrm{CF}}-(q\xi_{\|\pi})^2. \tag{B10}$$

The location of the spinodal is determined by the condition

$$A_{\mp}(q\xi_{\parallel\pi})=M(p_{\beta}B_{s\pm},q\xi_{\parallel\pi}), \tag{B11}$$

where A_- is the upper, and A_+ is the lower spinodal. Expanding the rhs of the above equation up to term linear in ΔB and substituting $B_{s\pm}$ [solutions of Eq. (B10)] into Eq. (B11) we obtain

$$A_-(q\xi_{\parallel\pi})-A_+(q\xi_{\parallel\pi})=\frac{1}{(q\xi_{\parallel\pi})^2_{\mathrm{CF}}}\sqrt{\frac{8}{f'''(p_{\beta}B_i)}}\times[(q\xi_{\parallel\pi})^2_{\mathrm{CF}}-(q\xi_{\parallel\pi})^2]^{3/2}. \tag{B12}$$

Next, we determine the free energy of the system close to the critical filling point. We expand the Hamiltonian (6.1) around B_i up to square terms in $\Delta B_{\pm}$,

$$\mathcal{H}(l_0(p_{\beta}B),p_{\beta}B,q\xi_{\parallel\pi})=\mathcal{H}(l_0(p_{\beta}B_i),p_{\beta}B_i,q\xi_{\parallel\pi})+\frac{1}{2}\frac{d^2\mathcal{H}}{d(p_{\beta}B)^2}(p_{\beta}B_i,q\xi_{\parallel\pi})\times(p_{\beta}\Delta B_{\pm})^2 \tag{B13}$$

With the help of Eq. (B7) we obtain

$$\mathcal{H}(p_{\beta}B,q\xi_{\parallel\pi})=\mathcal{H}(p_{\beta}B_i,q\xi_{\parallel\pi})-\frac{3}{f'''(p_{\beta}B_i)(q\xi_{\parallel\pi})^2_{\mathrm{CF}}}[(q\xi_{\parallel\pi})^2_{\mathrm{CF}}-(q\xi_{\parallel\pi})^2]^2. \tag{B14}$$

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[48] The expression given in Eq. (3.1),

$$l(x)=l_\pi+B_{1,0}\cos qx+B_{2,0}\cos^2 qx+B_{0,1}\sin^2 qx+B_{3,0}\times\cos^3 qx+B_{1,1}\cos qx\sin^2 qx+\cdots,$$

can be rewritten in an equivalent form

$$l(x)=l_\pi+\Delta_1+(B_{1,0}+\Delta_2)\cos qx+(B_{2,0}-\Delta_1)\cos^2 qx+(B_{0,1}-\Delta_1)\sin^2 qx+(B_{3,0}-\Delta_2)\cos^3 qx+(B_{1,1}-\Delta_2)\cos qx\sin^2 qx+\cdots,$$

where $\Delta_1,\Delta_2,\dots,$ are arbitrary numbers. This transformation does not change $l(x)$ and resembles the gauge transformation in electrodynamics. Δ_1, Δ_2 can be chosen in such a (unique) way that the sinus functions do not appear in the expansion (3.1). The linearization breaks this gauge symmetry; it is an additional argument against the linearization procedure.

[49] $\Phi(s)$ is an even function of s, as follows from Eq. (4.4). The expression given in Eq. (4.5) has to be an even function as well. It is a simple consequence of the following identity:

$$F(\alpha,\gamma,-s)=F(\gamma-\alpha,\gamma,s).$$

[50] Instead of integrating step by step function $\exp(-p_\beta B\cos qx)$ we can transform its integral into the Bessel integral

$$K_0(s)=\frac{1}{2\pi i}\oint\frac{dz}{z}e^{(i\pi/2)(z-1/z)}=\frac{1}{\pi}\int_0^\pi d\varphi\, e^{-s\cos\varphi}.$$

This is a very particular case concerning short-range, purely exponential effective interaction potential. In a general case there is no other way leading to the Hamiltonian $\mathcal{H}(l_0,B)$ than integrating step by step the potential $\omega(l_0+B\cos qx)$.

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