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Critical effects at complete wetting

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The approach towards complete wetting is considered for adsorbed liquid layers and for gravity-thinned layers in binary mixtures. These layers are bounded by one or two fluid-fluid interfaces. The thermal fluctuations of those interfaces are studied in the framework of effective interfacial models. Their correlation function $C(x)$ is calculated within the Ornstein-Zernike approximation and by transfer-matrix methods. For large distances x, $C(x) \propto \exp(-x/\xi_{\parallel})$. Due to the divergence of the correlation length $\xi_{\parallel}$, complete wetting can be regarded as a critical phenomenon. Two different scaling regimes have to be distinguished depending on the nature of the long-ranged forces and on the dimensionality. In the mean-field regime, the critical exponents depend on the long-ranged forces. In the fluctuation-dominated regime, they depend only on the dimensionality. It is also shown that these critical effects are characterized by one superuniversal feature: The critical exponent η which governs the decay of the correlation function $C(x)$ for $x \ll \xi_{\parallel}$ is zero both in the mean-field and in the fluctuation-dominated regime. The result $\eta = 0$ is expected to be valid for all types of wetting transitions. The experimental work which has focused on the thickness of the wetting layer is briefly reviewed. Furthermore, two types of experiments are proposed by which the correlation length $\xi_{\parallel}$ could be observed: it should show up both in the intensity of the small-angle scattering of light from the interfaces and in experiments which measure the dispersion relation of the capillary waves. This relation is found to be $\omega^2(q) \propto q(q^2 + \xi_{\parallel}^{-2})$, where ω and q are the frequency and the wave number of such waves. It is also suggested that the regime of critical wetting could be obtained in binary mixtures by the addition of impurities.

I. INTRODUCTION

Complete wetting has been recently studied in two different physical systems: (1) in the adsorption of liquids on substrate surfaces;[1–8] and (2) in binary liquid mixtures in contact with their vapor[9–12] or with a surface which prefers one of the two liquid phases.[13,14] The wetting layers observed in these systems are bounded by two interfaces. In the case of adsorption or binary mixtures in contact with a selective surface, the wetting layer is bounded by a solid-liquid and a fluid-fluid interface. In the case of a binary mixture in contact with its vapor, the boundaries consist of two fluid-fluid interfaces. The critical effects at wetting can be understood in terms of the effective interactions between these two interfaces.

For complete wetting, this interaction is described by an effective potential which has been known for a long time.[15–17] This potential yields a prediction for the thickness $\bar{l}$ of the wetting layer.[15–17] That quantity has indeed been studied in many experiments.[1–14] On the other hand, it has been largely overlooked by the wetting community that the same effective potential implies *long-range interfacial correlations*[18–22] if the wetting layer is bounded by at least one fluid-fluid interface.[23–25] Due to these correlations, complete wetting involves the additional length scale $\xi_{\parallel}$, which governs the correlations parallel to the interfaces. Because of $\xi_{\parallel}$, *complete* wetting can be regarded as a critical phenomenon. That is the main point of this paper. This viewpoint becomes especially clear when complete wetting is studied for arbitrary dimensionality (see Secs. IV and V). For three-dimensional systems, on the other hand, where complete wetting has already been observed, the correlation length $\xi_{\parallel}$ should be accessible to various types of experiments (see Sec. VI).

Most of the recent theoretical work has been focused on *critical* rather than on complete wetting.[26,27] From these theoretical efforts, a rather complex picture has emerged for bulk dimension $d = 3$. For short-range forces, critical wetting has been found,[28,29] and effective interface potentials have been obtained which seem to lead to an intriguing and nonuniversal critical behavior.[30–34] Such a behavior might have been observed in a Monte Carlo simulation.[35] For systems with long-range forces, critical wetting is less likely to occur.[36] In the case of adsorption, the present theoretical picture is as follows. If the adatom-substrate interactions are long ranged and the adatom-adatom interactions are short ranged, the square-gradient approximation for the density functional of the fluid is appropriate and one may study a Landau-Ginzburg type of theory for the fluid density.[19,37] As a result, one obtains an effective interface potential which implies that a critical wetting transition cannot occur as a function of temperature.[18,19,36–38] If both the adatom-substrate and the adatom-adatom interactions are long ranged, such a transition might occur,[39–43] but only if the effective potential fulfills several restrictive constraints. As a consequence, *fine tuning* of the microscopic interaction parameters is necessary in this case. Thus, it is not surprising that no clear experimental evidence has been found for critical wetting so far.

On the other hand, when viewed as critical phenomena, complete wetting and critical wetting are quite similar. They share indeed most of their critical features: (1) the length scales $\bar{l}$ and $\xi_{\parallel}$ diverge; (2) thermodynamic quantities such as the interfacial specific heat have a singular behavior; (3) these critical effects can be characterized by critical exponents; (4) these exponents are universal and depend only on the bulk dimensionality and on the short- or long-ranged nature of the underlying microscopic interactions; and (5) there are scaling laws which reduce the number of independent critical exponents. In fact, from this conceptual point of view, complete and critical wetting differ only in this number: complete wetting can be characterized by one independent exponent,[18,19] whereas critical wetting is governed by two such exponents.[44–46] Therefore, complete wetting can be considered as a protocritical transition. (The expression "protocritical" has been used before for the bulk critical behavior of the Yang-Lee edge singularity.[47])

For short-range forces, the critical effects at complete wetting have been studied by various methods. Within mean-field theory, the thickness $\bar{l}$ has been found to diverge logarithmically,[48,49] whereas the correlation length $\xi_{\parallel}$ exhibits a power-law divergence.[18,19(a),22] A simple Ginzburg criterion suggests that these results should apply for three-dimensional systems.[18,33] This is in accordance with a linear renormalization-group calculation as reported in Ref. 18. The logarithmic divergence of $\bar{l}$ as predicted by mean-field theory has indeed been observed in a recent Monte Carlo simulation for a three-dimensional system with short-range forces.[50] For two-dimensional systems, both $\bar{l}$ and $\xi_{\parallel}$ have a power-law divergence which has been obtained from continuous[46,51] and discrete[52,53] interface models.

In the present paper, complete wetting is systematically studied for d-dimensional systems with long-range forces. The results for short-range forces are recovered as a limiting case. This work which is an elaboration on Ref. 18 is done in the framework of effective interface models. In Sec. II, these models are motivated and defined. In particular, it is shown that both adsorbed liquid layers and gravity-thinned layers in binary mixtures can be studied within the same theoretical framework. In Sec. III, complete wetting is investigated by mean-field theory and by the Ornstein-Zernike approximation for the interfacial correlations. Section IV contains a rather extensive study of complete wetting in two-dimensional systems. The reader who is not interested in the more formal aspects of this work may skip both Secs. III and IV since their main results are summarized at the beginning of Sec. V. That section contains a unified scaling picture for complete wetting. Finally, two types of experiments for the observation of the correlation length $\xi_{\parallel}$ are proposed in Sec. VI.

II. EFFECTIVE INTERFACE MODELS

A. Adsorbed liquid layers

First, consider a fluid of adatoms in the presence of a substrate surface. Due to the attractive interactions between the adatoms and the solid, a liquid layer may be formed on the substrate although the bulk fluid is still in its vapor phase. The thickness of this wetting layer grows as one gets closer to the bulk coexistence curve of the fluid. Finally, at coexistence, the wetting layer is macroscopically thick, and the solid is completely wet. This implies that the interfacial tensions σ_{SL}, σ_{SV}, and σ_{LV} satisfy Antonow's rule $\sigma_{SL}+\sigma_{LV}=\sigma_{SV}$,[54] where the subscripts S, L, and V stand for solid, liquid, and vapor.

On a microscopic scale, the two interfaces which bound the wetting layer have an intrinsic structure as described by the density profile of the fluid. Near the surface of the solid, the fluid density exhibits oscillations due to packing effects.[40] Typically, these oscillations are confined to a few interatomic spacings from the substrate. Within the liquid-vapor interface, on the other hand, the density is expected to vary smoothly from its value in the liquid to its value in the vapor. The scale for this variation and, thus, for the intrinsic width of the liquid-vapor interface, is given by the bulk correlation length ξ_b.

In this work, the mean value $\bar{l}$ for the thickness of the wetting layer is always assumed to be large compared to both the interatomic spacings and the bulk correlation length ξ_b.[55] In this regime, a coarse-grained description should be appropriate where the intrinsic structure of the interfaces is neglected. On this coarse-grained scale, the solid-liquid interface is viewed as a geometric surface, and the liquid-vapor interface as a structureless drumhead. As a consequence, the wetting layer is described by a single variable l which measures the distance between the two interfaces (see Fig. 1). In general, this distance deviates from its mean value $\bar{l}$ due to thermal fluctuations of the liquid-vapor interface, i.e., due to *capillary waves.* Thus, the distance l is a fluctuating field which depends on the coordinates $\mathbf{x}=(x_1,x_2)$ parallel to the substrate surface: $l=l(\mathbf{x})$; see Fig. 1(b).

Note that the description of the wetting layer in terms of a single-valued variable l does not include extreme thermal fluctuations which lead to overhangs of the interface. However, as long as one stays away from any bulk critical point, such fluctuations should be rather rare. Indeed, the typical capillary waves are expected to be small-amplitude waves which means that their amplitude is small compared to their wavelength. In the *absence* of a substrate, the capillary waves on a liquid-vapor interface have been theoretically studied in much detail.[56,57,54] However, as shown in this paper, the properties of these waves are strongly affected by the presence of a substrate

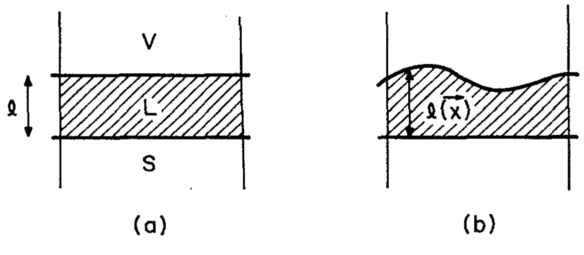

FIG. 1. Wetting layer of adsorbed liquid (L) between solid (S) substrate and the vapor (V) phase. In (a), the thickness l of this layer is constant; in (b), it varies due to thermal fluctuations of the liquid-vapor interface. $\mathbf{x}$ denotes the coordinates parallel to the the solid-liquid interface.

or any other interface which interacts with the liquid-vapor one.

What is the free energy associated with a wetting layer of thickness $l(\mathbf{x})$ as shown schematically in Fig. 1? First consider a layer of *constant* thickness l as in Fig. 1(a). Its free energy per unit area will be referred to as the effective interface potential $V(l)$. This potential can be derived from microscopic considerations where one starts from the interactions between the single atoms. The adsorption systems studied experimentally in Refs. 1–8 are governed by dispersion or van der Waals forces, i.e., by induced-dipole–induced-dipole interactions. If retardation effects are neglected, the dispersion force between two atoms has a long-range attractive tail $\propto r^{-6}$, where $r \equiv |\mathbf{r}|$ is the separation between the atoms.[15,16] To be more specific, assume that the tails of the solid-fluid interactions $w_{SF}(r)$ and the fluid-fluid interactions $w_{FF}(r)$ are given by

$$\begin{aligned} w_{SF}(r) &\to -\epsilon_{SF}(r/\lambda_{SF})^{-6} , \\ w_{FF}(r) &\to -\epsilon_{FF}(r/\lambda_{FF})^{-6} , \end{aligned} \tag{2.1}$$

for large r. The ϵ's and λ's in (2.1) are the parameters for the interaction energies and for the interaction ranges, respectively. It can be shown[39] that (2.1) leads to an effective interface potential

$$V(l) = \delta\mu\, l + V_{SF}(l) + V_{FF}(l) \tag{2.2}$$

with the asymptotic behavior

$$V_{SF}(l) + V_{FF}(l) \to W l^{-2} \tag{2.3}$$

for large l. The variable $\delta\mu$ in (2.2) is given by

$$\delta\mu = (\rho_L - \rho_V)(\mu^* - \mu) , \tag{2.4a}$$

where ρ_L and ρ_V are the particle number densities of the liquid and the vapor, and $\mu^* - \mu$ is the deviation of the chemical potential μ from its value μ^* at coexistence. If the vapor is treated as an ideal gas, and if one considers thermodynamic paths with constant temperature, one has

$$\mu^* - \mu = -k_B T \ln(p/p^*) , \tag{2.4b}$$

where p is the vapor pressure and p^* is its value at coexistence. The Hamaker constant W in (2.3) can be expressed in terms of the microscopic parameters which enter (2.1). One finds[39,27]

$$W = \frac{\pi}{12}(\rho_L - \rho_V)(\rho_S \epsilon_{SF} \lambda_{SF}^6 - \rho_L \epsilon_{FF} \lambda_{FF}^6) , \tag{2.5a}$$

where ρ_S is the particle number density of the solid. This formula may be further simplified if one takes $\epsilon_{SF} \simeq \epsilon_{FF} \simeq \epsilon$ and $\lambda_{SF} \simeq \lambda_{FF} \simeq \lambda$. This leads to

$$W = \frac{\pi}{12}(\rho_L - \rho_V)(\rho_S - \rho_L)\epsilon\lambda^6 . \tag{2.5b}$$

The empirical value for W is

$$W \sim k_B \times (100\ \mathrm{K}) \sim 10^{-14}\ \mathrm{erg} , \tag{2.6}$$

as obtained, for instance, from the data of Ref. 1.

In the classical theories,[15,16] the mean value $\bar{l}$ for thickness of the wetting layer is determined by the minimum of the effective potential $V(l)$, i.e., by

$$0 = \left.\frac{\partial V}{\partial l}\right|_{l=\bar{l}} \simeq \delta\mu - 2W\bar{l}^{-3} . \tag{2.7}$$

Thus, the mean position $\bar{l} \propto (\delta\mu)^{-1/3}$.[15,16] Such a behavior has been seen in many experiments,[1–3,5,7,8] although the value for the exponent is often found to be larger than $\frac{1}{3}$ (see the discussion in Sec. VI A).

Next, consider thermal fluctuations of the liquid-vapor interface. Such fluctuations increase the free energy of the wetting layer due to (i) *distortions* of the liquid-vapor interface, and (ii) *displacements* of this interface from its mean position $\bar{l}$. The free-energy increase due to distortions of the interface is given by the interfacial tension $\sigma \equiv \sigma_{LV}$ times the increase in the interfacial area, i.e., by

$$\sigma \int d^2x \{[1 + (\nabla l)^2]^{1/2} - 1\} = \int d^2x [\tfrac{1}{2}\sigma(\nabla l)^2 + O((\nabla l)^4)] . \tag{2.8}$$

The square-gradient approximation is physically motivated by the fact that the capillary waves are expected to be small-amplitude waves. This approximation may also be justified by more formal arguments. The free-energy increase due to the displacements of the interface is taken to be

$$\int d^2x [V(l(\mathbf{x})) - V(\bar{l})] , \tag{2.9}$$

where the effective potential $V(l)$ is given by (2.2). For the first two terms of $V(l)$ in (2.2), the expression (2.9) is strictly valid since these terms arise from external potentials for the fluid molecules which do not depend on the configurations of these particles. In contrast, the last term $V_{FF}(l)$ in (2.2) stems from the microscopic interactions *between* the fluid molecules. For an $\mathbf{x}$-dependent interface position $l(\mathbf{x})$, these interactions give rise *both* to a contribution $V_{FF}(l(\mathbf{x}))$ in (2.9) *and* to the distortion term (2.8). In addition, one would expect more complicated terms which involve products of l and $(\nabla l)^2$. Such terms will not be considered here. They would not affect the mean-field results discussed in Sec. III, but could have some effect in the fluctuation-dominated regime.

Thus, the total free energy $F\{l\}$ for a thermal fluctuation $l(\mathbf{x})$ is taken to be

$$F\{l\} = \int d^2x [\tfrac{1}{2}\sigma(\nabla l)^2 + V(l)] . \tag{2.10}$$

As a consequence, the probability P for such a fluctuation is given by

$$P\{l\} \propto e^{-F\{l\}/(k_B T)} , \tag{2.11a}$$

where k_B and T are the Boltzmann constant and the temperature. Once $P\{l\}$ is specified, all interfacial properties may be expressed in terms of Feynman path integrals over l. For instance, the interfacial free energy f_s is

$$f_s = -k_B T \ln\left[\iint \mathcal{D}\{l\} P\{l\}\right] , \tag{2.11b}$$

and the mean thickness $\bar{l}$ of the wetting layer is

$$\bar{l} = \iint \mathcal{D}\{l\} P\{l\} l . \tag{2.11c}$$

Note that the expectation values of l are not affected by any constant term in $V(l)$ since such a term can be absorbed in the normalization of $P\{l\}$.

The effect of gravity has not been included in the effective potential (2.2). Its influence on the thickness $\bar{l}$ is difficult to estimate in general since it depends on the geometry of the adsorption experiment. Gravity also affects the fluctuations of the liquid-vapor interface.

$$V_g(l)=\tfrac{1}{2}(\rho_L-\rho_V)mg(l-\bar{l})^2$$

$$\equiv\tfrac{1}{2}\sigma[(l-\bar{l}/\kappa)]^2 \qquad (2.12)$$

for the effective potential, where m, g, and κ are the particle mass, the gravitational acceleration, and the capillary length, respectively. This term will be considered in Sec. VI A.

B. Gravity-thinned layers in binary mixtures

The second class of systems where complete wetting has been studied experimentally consists of binary liquid mixtures.[9–14] As the temperature is changed, these systems move along their line of triple points where the vapor coexists with the two liquid phases, say with the A and B phase. If the mass density $\bar{\rho}_B$ of the B phase is larger than the mass density $\bar{\rho}_A$ of the A phase, the lighter A phase will normally sit on top of the heavier B phase due to the presence of gravity. It can happen, however, that a wetting layer of the heavier B phase intrudes between the vapor and the A phase[9–12] as shown schematically in Fig. 2(a). This wetting layer will be referred to as the V-B-A layer. A different geometry may occur in the presence of a solid surface which prefers the lighter A phase.[13,14] In this case, a wetting layer of the lighter A phase can be formed between the solid surface and the heavier B phase. Such a S-A-B layer is shown schematically in Fig. 2(c). This is in fact the geometry studied in Ref. 14.

Let us first consider a V-B-A wetting layer of constant thickness l as shown in Fig. 2(a). Obviously, this situation looks very similar to the one discussed in the preceding subsection [see Fig. 1(a)]. The free energy per unit area of such a wetting layer is given by[17]

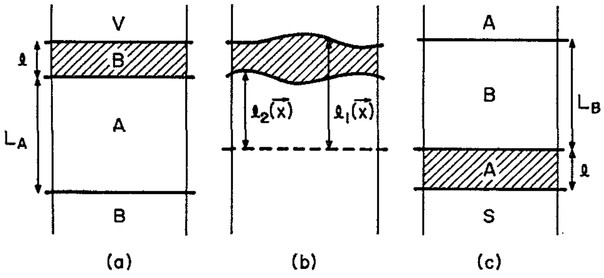

FIG. 2. Geometry for gravity-thinned layers in binary mixtures. A is the lighter and B the heavier liquid phase of the mixture. (a) and (b), wetting layer of the heavier B phase between the vapor (V) and the A phase (Refs. 9–12). The variables l_1 and l_2 denote the local distance of the two fluid-fluid interfaces from some reference plane. (c), wetting layer of the lighter A phase between the solid (S) wall and the B phase (Ref. 14).

$$V(l)=(\bar{\rho}_B-\bar{\rho}_A)gL_Al+Wl^{-2} \qquad (2.13)$$

for l large compared to the interatomic spacings. $\bar{\rho}_A$ and $\bar{\rho}_B$ are the mass densities of the two phases, and L_A is the thickness of the A phase [see Fig. 2(a)]. The first term in (2.13) is the work one has to do against gravity in order to move the layer of the B phase from the bottom to the top of the A phase. The second term in (2.13) is due to the underlying dispersion forces between the molecules. According to de Gennes,[17] the Hamaker constant W is given by

$$W=\frac{\pi}{12}(\alpha_B-\alpha_A)(\alpha_V-\alpha_B)\ , \qquad (2.14)$$

where the α's are proportional to the specific polarizabilities of the three phases. A similar expression can be obtained from (2.5b) if one identifies the solid, liquid, and vapor in the adsorption problem with the vapor, liquid B, and liquid A in the binary mixture. This leads to

$$W=\frac{\pi}{12}(\rho_B-\rho_A)(\rho_V-\rho_B)\epsilon\lambda^6\ , \qquad (2.15)$$

where ρ_A, ρ_B, and ρ_V are the particles' number densities. ϵ and λ may be thought of as an average energy and an average range parameter for the three possible pairs of molecules in the binary mixture. The free energy of an S-A-B layer as shown in Fig. 2(c) can be easily found from (2.13) and (2.15) by a proper identification of the various phases involved. In this way, one finds

$$V(l)=(\bar{\rho}_B-\bar{\rho}_A)gL_Bl+Wl^{-2}\ . \qquad (2.16a)$$

L_B is the thickness of the intermediate B phase, and

$$W=\frac{\pi}{12}(\rho_A-\rho_B)(\rho_S-\rho_A)\epsilon\lambda^6 \qquad (2.16b)$$

may be taken as an approximate expression for the Hamaker constant of a gravity-thinned layer due to a selective surface.

Note that the first term in (2.13) and (2.16a) depends on the *mass* densities $\bar{\rho}_A,\bar{\rho}_B$, whereas the expressions (2.15) and (2.16b) for W depend on the *number* densities ρ_A,ρ_B. For complete wetting, one needs $W>0$. Thus, ρ_A should be *larger* than ρ_B since one would expect that $\rho_V<\rho_B$ in (2.15) and $\rho_A<\rho_S$ in (2.16b). On the other hand, $\bar{\rho}_A$ has to be *smaller* than $\bar{\rho}_B$ in order to have a gravity-thinned layer. It turns out that both inequalities hold for most of those mixtures for which a wetting layer has been observed. This will be discussed in more detail in Sec. VI B.

Next, consider thermal fluctuations of the interfaces which bound the wetting layer. One may apply the same philosophy as in the case of adsorbed layers if one makes two simplifying assumptions. First, the lower B phase in Fig. 2(a) and the upper A phase in Fig. 2(c) are assumed to be so large that they effectively act as infinite reservoirs for the wetting layers. This leads to a description where the possible values for l are not restricted. The second assumption, on the other hand, relies on the fact that

$l \ll L_A$ or L_B. As a consequence, one may consider L_A and L_B to be constant and ignore their fluctuations. The latter assumption will be justified in Sec. VI B. If one makes those two assumptions, the free energy $F\{l\}$ for the S-A-B layer has exactly the same form as (2.10), with the interfacial tension $\sigma = \sigma_{AB}$ and the effective potential $V(l)$ now given by (2.16). For the V-B-A layer [see Fig. 2(a)], the situation is slightly more complicated since this wetting layer is bounded by two fluid-fluid interfaces which can both fluctuate.[58] Therefore, one has to introduce two variables $l_1(\mathbf{x})$ and $l_2(\mathbf{x})$ which measure the distance of these interfaces from some reference plane [see Fig. 2(b)]. In order to emphasize the analogy with the S-A-B geometry [see Fig. 2(c)], it is useful to choose this reference plane to be equal to the mean position $\bar{l}_1$ of the B-V interface.

The free-energy functional now has the form

$$F\{l_1,l_2\} = \int d^2x\left[\tfrac{1}{2}\sigma_1(\nabla l_1)^2 + \tfrac{1}{2}\sigma_2(\nabla l_2)^2 + V(l_2 - l_1)\right] , \tag{2.17}$$

with the interfacial tensions $\sigma_1 = \sigma_{BV}$ and $\sigma_2 = \sigma_{AB}$. The effective potential $V(l)$ in (2.17) is given by (2.13). The free energy (2.17) can be brought into a simpler form by the linear transformation[59]

$$l_1 = \tilde{l} - \frac{\sigma_2}{\sigma_1+\sigma_2} l ,$$

$$l_2 = \tilde{l} - \frac{\sigma_1}{\sigma_1+\sigma_2} l .$$

This leads to

$$F\{l_1,l_2\} = F\{l\} + \int d^2x\left[\tfrac{1}{2}\tilde{\sigma}(\nabla \tilde{l})^2\right] , \tag{2.18}$$

with

$$F\{l\} = \int d^2x\left[\tfrac{1}{2}\sigma(\nabla l)^2 + V(l)\right] , \tag{2.19}$$

where $\sigma = \sigma_1\sigma_2/(\sigma_1+\sigma_2)$ and $\tilde{\sigma} = \sigma_1 + \sigma_2$. Note that the free energy (2.19) for the V-B-A layer also has the same form as the corresponding free energy (2.10) for adsorbed liquid layers.

The free energy (2.18) does not contain a potential term for the "center-of-mass" variable

$$\tilde{l} = (\sigma_1 l_1 + \sigma_2 l_2)/(\sigma_1 + \sigma_2) .$$

Thus, the fluctuations of $\tilde{l}$ seem to be unrestricted. However, these fluctuations are bounded by the additional term

$$V_g(l_1) = \tfrac{1}{2}\sigma_1\kappa_1^{-2}(l_1 - \bar{l}_1)^2 \tag{2.20}$$

due to gravity which has been neglected in (2.17). κ_1 is the capillary length of the B-V interface, and its mean position $\bar{l}_1 = 0$ due to above convention for the reference plane. A term such as (2.20) should always be included for a liquid-vapor interface in a gravitational field irrespective of the possible internal structure the liquid might have. This term will be considered in Sec. VI B.

C. Generalized models

It is useful to generalize the interface models discussed in the preceding subsections in two ways:[18] (1) From a conceptual point of view, it is very instructive to consider arbitrary dimensionality. Thus, $(d-1)$-dimensional interfaces in d-dimensional systems will be considered. (2) The l^{-2} term of the effective potential $V(l)$ will be generalized to an arbitrary power l^{-p}.

The l^{-2} term stems from nonretarded dispersion forces in three-dimensional systems. For two-dimensional systems, the same kind of forces will lead to a term proportional to l^{-3}.[46] The latter l-dependence is also obtained in $d=3$ dimension if retardation effects are included.[16,60] An arbitrary power l^{-p} can be derived from a microscopic adsorption model where the solid-fluid and the fluid-fluid interactions w_{SF} and w_{FF} behave as [cf. (2.1)]

$$w_{SF}(r) \to -\epsilon_{SF}(r/\lambda_{SF})^{-q} ,$$
$$w_{FF}(r) \to -\epsilon_{FF}(r/\lambda_{FF})^{-q} \tag{2.21}$$

for large separations r between the atoms or molecules. At the coexistence curve of the bulk fluid, this leads to an effective interface potential $V(l)$ with the asymptotic behavior

$$V(l) \to Wl^{-p} , \quad p = q - d - 1 \tag{2.22}$$

for large l with the generalized Hamaker constant[39]

$$W = \gamma(\rho_L - \rho_V)(\rho_S\epsilon_{SF}\lambda_{SF}^q - \rho_L\epsilon_{FF}\lambda_{FF}^q) , \tag{2.23}$$

where

$$\gamma \equiv \frac{\pi^{(d-1)/2}\Gamma((q-d-1)/2)}{(q-d-1)(q-d)\Gamma(q/2)} .$$

For nonretarded dispersion forces ($q=6$) in $d=3$ dimensions, this expression reduces to (2.5).

For small l, the effective potential $V(l)$ goes to some constant, the value of which depends on the details of the microscopic interactions w_{SF} and w_{FF}. The behavior of $V(l)$ for large and for small l may be combined into a term of the form $W(l+l_0)^{-p}$. l_0 is a nonuniversal parameter which is chosen in such a way that $V(0^+) = Wl_0^{-p}$. In addition, one must keep in mind that l measures the distance between the two interfaces. These interfaces may touch but cannot intersect each other. Thus, *l cannot be negative.* As a consequence, $V(l)$ contains a hard wall at $l=0^-$, i.e., $V(l) = \infty$ for $l<0$. This applies equally well to adsorbed and to gravity-thinned layers.

Thus, the free energy for the wetting layer is taken to be

$$F\{l\} = \int d^{d-1}x\left[\tfrac{1}{2}\sigma(\nabla l)^2 + V(l)\right] , \tag{2.24a}$$

with

$$V(l) = \begin{cases} \infty , & l<0 \\ \delta\mu\, l + W(l+l_0)^{-p} , & l>0 . \end{cases} \tag{2.24b}$$

For adsorbed layers, $\delta\mu$ is given by (2.4). For gravity-thinned layers, $\delta\mu$ has to be identified with $(\bar{\rho}_B - \bar{\rho}_A)gL$; see (2.13) above.

The model (2.24) is appropriate for complete wetting, which is the topic of the present paper. Critical wetting, on the other hand, occurs when W is negative and goes to zero from below as a function of temperature.[39] That this may happen can be seen from (2.23). Assume that W is negative due to the third factor in (2.23) for temperatures T far away from the bulk critical temperature T_c of the fluid. This implies that the solid is only incompletely wet by the fluid. As T is increased towards T_c, the liquid density ρ_L decreases and, as a consequence, the third factor in (2.23) may vanish at some wetting temperature $T_w < T_c$. The universal aspects of critical and multicritical wetting transitions in systems with long-range forces are investigated in a different paper.[43]

III. MEAN-FIELD THEORY AND ORNSTEIN-ZERNIKE APPROXIMATION

The simplest method by which the interface model (2.24) can be investigated is mean-field (MF) theory.[15–18] As mentioned above [see (2.7)], the mean value $\bar{l}$ of the wetting layer thickness is determined within MF theory from

$$\frac{\partial V}{\partial l} = 0 \, . \tag{3.1}$$

In the following, the MF value for $\bar{l}$ will be denoted by $\hat{l}$. For the effective potential (2.24b), (3.1) yields

$$\hat{l} \propto (\delta\mu)^{-1/(1+p)} \, . \tag{3.2}$$

As a consequence, the interfacial free energy f_s has a singular part[18]

$$f_s = V(\hat{l}) \propto (\delta\mu)^{p/(1+p)} \, . \tag{3.3}$$

Next, consider small fluctuations of l around $l = \hat{l}$. Within the Ornstein-Zernike (OZ) approximation, these fluctuations are governed by the Gaussian expression

$$F\{l\} = F\{\hat{l}\} + \int d^{d-1}x \left[\tfrac{1}{2}\sigma(\nabla\delta)^2 + \tfrac{1}{2}\sigma\xi_\parallel^{-2}\delta^2\right] + O(\delta^3) \tag{3.4a}$$

for the deviations

$$\delta \equiv l - \hat{l} \, , \tag{3.4b}$$

with

$$\sigma\xi_\parallel^{-2} \equiv \left. \frac{d^2V(l)}{dl^2} \right|_{l=\hat{l}} \, . \tag{3.4c}$$

As shown below, $\xi_\parallel$ as defined by (3.4c) is the MF expression for the correlation length parallel to the interfaces. From (3.4c) and (2.24b), one finds that this quantity behaves as[18]

$$\xi_\parallel \propto (\delta\mu)^{-(2+p)/(2+2p)} \, . \tag{3.5}$$

On physical grounds, the wavelength of the interface fluctuations described by the continuum model (3.4) should be large compared to the intrinsic thickness of the two interfaces (see Sec. II A). Otherwise, the description of the interfaces in terms of smooth drumheads is not justified. As a consequence, one has to supplement the continuum model (3.4) with a high-momentum cutoff $1/a$. A reasonable choice might be to take $a \gtrsim 10\times$(interatomic spacing).[55]

From (3.4), one obtains the OZ expression for the correlation function

$$C(x) \equiv \langle [l(0)-\hat{l}][l(\mathbf{x})-\hat{l}] \rangle = \left. \frac{k_BT}{\sigma} \int \frac{d^{d-1}q}{(2\pi)^{d-1}} \frac{e^{i\mathbf{q}\cdot\mathbf{y}}}{q^2+\xi_\parallel^{-2}} \right|_{y^2=\bar{x}^2} \, , \tag{3.6a}$$

with[30]

$$\bar{x}^2 = x^2 + a^2 \, , \tag{3.6b}$$

where $1/a$ is the high-momentum cutoff introduced above. For $d \geq 3$, this cutoff is necessary in order that the integral in (3.6a) converges for large momenta q. For $d < 3$, this integral converges even for $a = 0$. Exactly the same expression as in (3.6) has been obtained for the correlation function of the soft mode in the density fluctuation near wetting.[19] Similar integrals arise for interface fluctuations in a weak gravitational field,[57] and in the Ornstein-Zernike theory for the correlations near a bulk critical point.[61,54]

The integral in (3.6) yields

$$C(x) = \bar{x}^{3-d}\Omega(\bar{x}/\xi_\parallel) = \xi_\parallel^{3-d} g(\bar{x}/\xi_\parallel) \, , \tag{3.7}$$

with

$$\Omega(z) = \frac{k_BT}{\sigma}(2\pi)^{(1-d)/2} z^{(d-3)/2} K_{(d-3)/2}(z) \, , \tag{3.8a}$$

$$g(z) = z^{3-d}\Omega(z) \, . \tag{3.8b}$$

$K_\nu(z)$ is a modified Bessel function.[62] Note that (3.7) gives a scaling form for $C(x)$: apart from an explicit prefactor, $C(x)$ depends only on the scaled coordinate $z \equiv \bar{x}/\xi_\parallel$. As a consequence, one can distinguish several regimes. $z \to 0$ corresponds to $x \lesssim a$, and $z \to \infty$ to $x \gg \xi_\parallel$. Near the transition where $\xi_\parallel$ is large, there is also an intermediate regime with $a \ll x \ll \xi_\parallel$. In the remaining part of this section, I will set $k_BT/\sigma \equiv 1$ in (3.8a).

First, consider the regime $x \gg \xi_\parallel$. For large z, the asymptotic behavior of K_ν is[62]

$$K_\nu(z) \to \left[\frac{\pi}{2z} \right]^{1/2} e^{-z} \text{ for all } \nu \, .$$

If this expression is inserted in (3.8), one finds[19]

$$C(x) \propto x^{1-d/2} e^{-x/\xi_\parallel} \tag{3.9}$$

for large x in *all* dimensions. The exponential decay in (3.9) shows that $\xi_\parallel$ as defined in (3.4) is indeed the correlation length for correlations parallel to the interface.

Next, consider the limiting behavior of the correlation function $C(x)$ for $x \to 0$. For small z,[62]

$$K_\nu(z) \to \begin{cases} \tfrac{1}{2}\Gamma(\nu)(z/2)^{-\nu} \, , & \nu \neq 0 \\ -\ln(z) \, , & \nu = 0 \, . \end{cases} \tag{3.10}$$

This yields

$$C(0)=\begin{cases}\Omega_0 a^{3-d}\,, & d>3\\ (1/2\pi)\ln(\xi_\parallel/a)\,, & d=3\\ g_0\xi_\parallel^{3-d}\,, & d<3\end{cases} \tag{3.11}$$

with

$$\Omega_0\equiv(2\pi)^{(1-d)/2}2^{(d-5)/2}\Gamma((d-3)/2)\,, \tag{3.12a}$$

$$g_0\equiv(2\pi)^{(1-d)/2}2^{(1-d)/2}\Gamma((3-d)/2)\,. \tag{3.12b}$$

Ω_0 and g_0 are the limiting values obtained from (3.8) for $d>3$ and $d<3$, respectively.

It follows from (3.11) that $C(0)$ diverges at complete wetting for $d\leq 3$.[19] This divergence has a very physical interpretation since $C(0)$ can be related to the effective interfacial thickness or roughness $\xi_\perp$:

$$\xi_\perp^2\equiv\langle(l-\hat{l})^2\rangle=C(0)\,. \tag{3.13}$$

Thus, the divergence of $C(0)$ implies that the interface becomes *rough* as the wetting layer becomes large. Note that a similar divergence occurs in the OZ theory for correlations near a bulk critical point in $d\leq 2$. In this case, the fluctuating field corresponds to a microscopic spin variable which can have only two possible values. As a consequence, the bulk correlation function $C_b(r)$ is bounded from above, and the divergence of $C_b(0)$ within the OZ theory is unphysical.[61] In the present context, however, the fluctuating field l can become arbitrarily large even in a microscopic model. Therefore, $C(x)$ is *not* bounded from above and the divergence of $C(0)$ as given by (3.11) can be interpreted in a physical way as is (3.13).

Since $C(0)$ becomes very large for $d\leq 3$, it is convenient to consider the difference correlation function

$$\begin{aligned}\Delta C(x)&\equiv C(0)-C(x)\\ &=\tfrac{1}{2}\langle[l(0)-l(\mathbf{x})]^2\rangle\,.\end{aligned} \tag{3.14}$$

This function has also been studied in the context of the roughening transition,[63] and for an interface in a weak gravitational field.[56] From the scaling form (3.7), one obtains for the difference correlation function

$$\begin{aligned}\Delta C(x)&=\xi_\parallel^{3-d}[g_0-g(\bar{x}/\xi_\parallel)]\\ &=\xi_\perp^2[1-\bar{g}(\bar{x}/\xi_\parallel)]\,,\end{aligned} \tag{3.15}$$

where (3.13) has been used in the last equation. Due to (3.9),

$$\Delta C(x)=\xi_\perp^2+O(e^{-x/\xi_\parallel})\ \text{as}\ x\to\infty\,, \tag{3.16}$$

whereas $\Delta C(x)\to 0$ as $x\to 0$ by definition.

So far, the asymptotic behavior of $C(x)$ for $x\to 0$ and for $x\to\infty$ has been discussed. Near the wetting transition, $\xi_\parallel$ diverges. The MF result for this divergence is given by (3.5). As a consequence, there is an intermediate x regime with $a\ll x\ll\xi_\parallel$. For $d\geq 3$, the behavior of $C(x)$ for such intermediate values of x follows again from (3.10). For $d>3$,

$$C(x)\to\Omega_0 x^{-(d-3)}\,, \tag{3.17}$$

with Ω_0 given by (3.12a), and, for $d=3$,

$$\Delta C(x)\to\frac{1}{4\pi}\ln(x/a)\,. \tag{3.18}$$

For $d<3$, the leading terms in (3.15) cancel, and one has to determine the next-to-leading term of the ascending series for $K_\nu(z)$. This term can be mostly easily obtained from the definition of $K_\nu(z)$ in terms of the modified Bessel functions $I_{\pm\nu}$, and from the ascending series for $I_{\pm\nu}$.[62] The form of this term depends on ν. For $0<\nu<1$, one obtains

$$K_\nu(z)=\tfrac{1}{2}\Gamma(\nu)(z/2)^{-\nu}+\tfrac{1}{2}\Gamma(-\nu)(z/2)^{\nu}$$

for $z\to 0$. If this expression is used in (3.15), one finds

$$\Delta C(x)=|\Omega_0|x^{3-d} \tag{3.19}$$

for $a\ll x\ll\xi_\parallel$. Ω_0 is again given by (3.12a). It is remarkable that the same prefactor, namely $|\Omega_0|$, occurs in (3.17) and in (3.19). In (3.17), Ω_0 arises from the leading term of the ascending series for $K_\nu(z)$. In (3.19), Ω_0 comes from the next-to-leading term of this series. Thus, OZ theory yields a scaling regime both for $d>3$ and for $d\leq 3$ where $C(x)$ and $\Delta C(x)$ are given by the same expression, $|\Omega_0|x^{3-d}$. The schematic behavior of $C(x)$ and $\Delta C(x)$ is shown in Figs. 3(a) and 3(b).

IV. COMPLETE WETTING IN TWO-DIMENSIONAL SYSTEMS

A. Transfer-matrix formalism

In bulk dimensionality $d=2$, the interface variable l depends only on one coordinate: $l=l(x)$. As a conse-

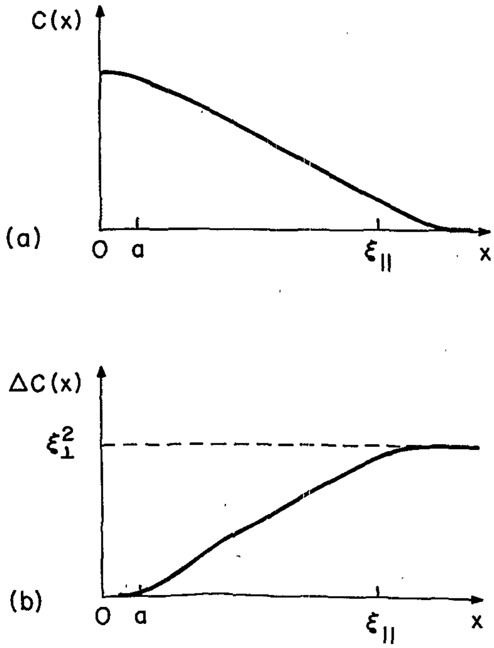

FIG. 3. (a) Correlation function $C(x)$ for the interfacial fluctuations in dimensionality $d>3$. (b) Difference correlation function $\Delta C(x)=C(0)-C(x)$ in $d\leq 3$. In the latter case, the interfacial roughness $\xi_\perp^2$ goes to infinity. In both (a) and (b), there is a scaling regime for intermediate x values with $a\ll x\ll\xi_\parallel$ (see text).

quence, the interface model (2.24) is one-dimensional and can be studied by transfer-matrix methods. For finite small-distance cutoff a, one has to determine the eigenvalues and eigenfunctions of the transfer matrix from an integral equation. In the limit $a \to 0$, this integral equation reduces to the Schrödinger-type equation[46,53,64]

$$H\psi_n(l) = \left[-\frac{1}{2\beta^2\sigma}\frac{d^2}{dl^2} + V(l) \right] \psi_n(l) = E_n \psi_n(l) , \tag{4.1}$$

where the "quantum-mechanical" potential $V(l)$ is given by (2.24b). Due to the hard wall at $l=0^-$, one has the boundary condition

$$\psi_n(0)=0 . \tag{4.2}$$

Note that $\beta \equiv 1/(k_B T)$ corresponds to Planck's constant, and the surface tension σ to the mass of the quantum-mechanical particle. For convenience, I will set $\beta \equiv 1$ and $\sigma \equiv 1$ in this section.

Within the transfer-matrix method, the physical quantities of interest can be expressed in terms of the eigenvalues and eigenfunctions of (4.1). The interfacial free energy f_s defined by (2.11b) is given by

$$f_s = E_0 = (\psi_0 \,|\, H\psi_0) . \tag{4.3}$$

E_0 is the ground-state energy and ψ_0 is the normalized ground-state wave function. The parentheses indicate a scalar product:

$$(f \,|\, g) \equiv \int_0^\infty dl\, f^*(l) g(l) .$$

The mean thickness $\bar{l}$ of the wetting layer is

$$\bar{l} = \langle l \rangle = (\psi_0 \,|\, l\psi_0) . \tag{4.4a}$$

For the potential (2.24b), one has the commutator relation $l = [\partial/\partial\delta\mu, H]$. This leads to[46]

$$\bar{l} = \frac{\partial E_0}{\partial \delta\mu} . \tag{4.4b}$$

The roughness $\xi_\perp$ of the interface is obtained from

$$\xi_\perp^2 = \langle (l-\bar{l})^2 \rangle = (\psi_0 \,|\, (l-\bar{l})^2 \psi_0) . \tag{4.5}$$

Finally, the correlation length $\xi_\parallel$ follows from the expression for the difference correlation functions [see (3.14)]

$$\begin{aligned} \Delta C(x) &= \tfrac{1}{2} \langle [l(0) - l(x)]^2 \rangle \\ &= \xi_\perp^2 - \sum_{n\,(>0)} e^{-(E_n - E_0)x} \,|\, (\psi_0 \,|\, l\psi_n) \,|^2 . \end{aligned} \tag{4.6}$$

For large separations x, the asymptotic behavior of this sum is governed by the first term with $n=1$. As a consequence,

$$\xi_\parallel = (E_1 - E_0)^{-1} . \tag{4.7}$$

Thus, in order to determine the critical behavior of the free energy f_s and the three diverging length scales $\bar{l}$, $\xi_\perp$, and $\xi_\parallel$, one has to find the eigenvalues E_0, E_1 and the ground state ψ_0 for the potential (2.24b). As shown below, the asymptotic behavior of these quantities can be obtained from two approximations for (2.24b). The first approximation consists of a harmonic potential plus a hard wall. This is discussed in the next subsection. The second approximation is given by the linear potential $v(l) = \delta\mu\, l$ plus the hard wall; see Sec. IV D. The harmonic approximation is correct for long-range forces with $p<2$, the linear approximation for $p>2$.

B. Harmonic approximation

If one expands the potential $V(l)$ as given by (2.24b) around its minimum at $l=\hat{l}$, one obtains

$$V(l) = V(\hat{l}) + \tfrac{1}{2}\omega^2 (l-\hat{l})^2 + \delta V(l) , \tag{4.8}$$

with

$$\delta V(l) \equiv \sum_{n=3}^{\infty} \frac{1}{n!} V^{(n)}(\hat{l}) (l-\hat{l})^n . \tag{4.9}$$

The expansion coefficients are

$$V^{(n)}(\hat{l}) = c_n \hat{l}^{\,-p-n} , \tag{4.10}$$

$$\omega = [V^{(2)}(\hat{l})]^{1/2} = (c_2)^{1/2} \hat{l}^{\,-(p+2)/2} , \tag{4.11}$$

where I have set l_0 in (2.24b) equal to zero for convenience. The harmonic approximation to $V(l)$ is obtained if one ignores the term $\delta V(l)$ in (4.8). Thus, one is left with the potential

$$V_H(l) = \begin{cases} \infty, & l<0 \\ V(\hat{l}) + \tfrac{1}{2}\omega^2 (l-\hat{l})^2, & l>0. \end{cases} \tag{4.12}$$

The corresponding eigenvalue problem,

$$\left[-\frac{1}{2}\frac{d^2}{dl^2} + V_H(l) \right] \varphi_n(l) = \epsilon_n \varphi_n(l) , \tag{4.13a}$$

$$\varphi_n(0) = 0 , \tag{4.13b}$$

can be solved in terms of parabolic cylinder functions[62,65] $D[\nu \,|\, x]$ (which are sometimes called Weber functions[66]). As a result, one finds

$$\varphi_n(l) = c_n D[\nu_n \,|\, (2\omega)^{1/2}(l-\hat{l})] , \tag{4.14}$$

with

$$\nu_n = -\tfrac{1}{2} + [\epsilon_n - V(\hat{l})]/\omega . \tag{4.15}$$

The normalization constant c_n in (4.14) is

$$c_n = (2\omega)^{1/4} \left[\int_{x_0}^{\infty} dx\, D^2[\nu_n \,|\, x] \right]^{-1/2} , \tag{4.16}$$

with

$$x_0 \equiv -(2\omega)^{1/2}\hat{l} = -[2(c_2)^{1/2}]^{1/2} \hat{l}^{\,(2-p)/4} . \tag{4.17}$$

The eigenvalues ϵ_n have to be obtained from the boundary condition $\varphi_n(0)=0$, which implies

$$D[\nu_n \,|\, x_0] = 0 , \tag{4.18}$$

with ν_n and x_0 given by (4.15) and (4.17). As $\delta\mu \to 0$, i.e., as complete wetting is approached, (4.17) leads to

$$x_0 \to \begin{cases} -\infty, & p<2 \\ -[2(c_2)^{1/2}]^{1/2}, & p=2 \\ 0, & p>2. \end{cases} \tag{4.19}$$

First, consider $p<2$ where $x_0 \to -\infty$. In this case, one can use the asymptotic behavior of $D[\nu \mid x]$ for large $|x|$:[67]

$$D[\nu \mid x_0] \approx e^{x_0^2/4} |x_0|^{-\nu-1} \left[\frac{\sqrt{2\pi}}{\Gamma(-\nu)} [1+A_\nu(x_0)] + \cos(\nu\pi) e^{-x_0^2/4} |x_0|^{2\nu+1} [1+B_\nu(x_0)] \right] \quad \text{as } x_0 \to -\infty . \tag{4.20}$$

Both $A_\nu(x_0)$ and $B_\nu(x_0)$ are $O(x_0^{-2})$, and $A_\nu(x_0)$ is positive. If one inserts (4.20) into (4.18), one obtains the limiting behavior

$$\nu_n \to n + \frac{1}{\sqrt{2\pi} n!} |x_0|^{2n+1} e^{-x_0^2/2} \quad \text{as } x_0 \to -\infty , \tag{4.21}$$

with $n=0,1,2,\dots$. The energies ϵ_n are related to ν_n by (4.15). This yields

$$\begin{aligned} \epsilon_n &= V(\hat{l}) + \omega(\nu_n + \tfrac{1}{2}) \\ &= V(\hat{l}) + \omega(n + \tfrac{1}{2}) + O(e^{-x_0^2}) \\ &\equiv \epsilon_n^\infty + O(e^{-x_0^2}) . \end{aligned} \tag{4.22}$$

Note that ϵ_n^∞ is the usual spectrum for an harmonic oscillator in an infinite system, i.e., without a wall. The correction terms due to the wall are exponentially small as $\delta\mu \to 0$ since $x_0^2 \propto \hat{l}^{(2-p)/2}$ and $\hat{l} \propto (\delta\mu)^{-1/(1+p)}$ from (3.2). As a consequence, the eigenfunctions $\varphi_n(l)$ of (4.13) also approach the eigenfunctions $\varphi_n^\infty(l)$ for an harmonic oscillator quite rapidly:

$$\begin{aligned} &\varphi_n(l) = \varphi_n^\infty(l) + O(e^{-x_0^2}) , \\ &\varphi_n^\infty(l) = \frac{2^{-n/2}}{\sqrt{n!}} \left[\frac{\omega}{\pi} \right]^{1/4} e^{-\omega(l-\hat{l})^2/2} H_n(\sqrt{\omega}(l-\hat{l})) , \end{aligned} \tag{4.23}$$

where $H_n(z)$ are the Hermite polynomials.[68] In particular, the ground state becomes

$$\varphi_0^\infty(l) = \left[\frac{\omega}{\pi} \right]^{1/4} e^{-\omega(l-\hat{l})^2/2} . \tag{4.24}$$

It is also instructive to study the difference correlation function $\Delta C(x)$ within the harmonic approximation. Using (4.22)–(4.24), one finds from (4.6) that

$$\Delta C(x) = \frac{1}{2\omega} \left[1 - \sum_{n\,(>0)} b_n^2 \exp(-a_n \omega x) \right] , \tag{4.25}$$

with

$$a_n = n + O(e^{-x_0^2}) , \tag{4.26a}$$

$$\begin{aligned} b_n &= \frac{2^{(1-n)/2}}{\sqrt{\pi n!}} \int_{-\infty}^{\infty} dx\, H_n(x) e^{-x^2} x + O(e^{-x_0^2}) \\ &= \begin{cases} 1 + O(e^{-x_0^2}), & n=1 \\ O(e^{-x_0^2}), & n \ge 2. \end{cases} \end{aligned} \tag{4.26b}$$

In the last equality, the recurrence relation[68] $dH_n(x)/dx = 2nH_{n-1}(x)$ for the Hermite polynomials has been used. Thus, apart from exponentially small corrections, only the term with $n=1$ contributes to the sum in (4.25).

So far, the harmonic approximation has been studied for long-range forces which are characterized by l^{-p} with $p<2$. For such values of p, the variable x_0 in (4.18) goes to minus infinity. For $p>2$, on the other hand, $x_0 \to 0^-$; see (4.19). As a consequence, one may expand the implicit equation (4.18) in powers of x_0. To leading order, this yields

$$\begin{aligned} 0 = {} & \cos(\pi\nu_n/2)\Gamma((\nu_n+1)/2) \\ & + \sqrt{2} x_0 \sin(\pi\nu_n/2)\Gamma((\nu_n+2)/2) , \end{aligned} \tag{4.27}$$

which implies

$$\nu_n = 2n + 1 - \frac{2\sqrt{2}}{\pi n!} \Gamma(n+\tfrac{3}{2}) |x_0| + O(x_0^2) . \tag{4.28}$$

If this is used in (4.15), one obtains, for the asymptotic behavior of the energies,

$$\begin{aligned} \epsilon_n &= V(\hat{l}) + \omega(\nu_n + \tfrac{1}{2}) \\ &= V(\hat{l}) + \omega(2n + \tfrac{3}{2}) + O(|x_0|) \\ &\equiv \epsilon_n^{\infty/2} + O(|x_0|) . \end{aligned} \tag{4.29}$$

$\epsilon_n^{\infty/2}$ is the spectrum for "one half of" an harmonic oscillator, i.e., for the potential

$$V_H^{\infty/2} = \begin{cases} \infty, & l < \hat{l}. \\ V(\hat{l}) + \tfrac{1}{2}\omega(l-\hat{l})^2, & l > \hat{l}. \end{cases} \tag{4.30}$$

C. Mean-field regime ($p<2$)

It turns out that the MF results discussed in Sec. III are correct even for $d=2$, provided that the exponent p in (2.24b) satisfies $p<2$. This will be shown below in two steps. First, it is shown that $E_n \to V(\hat{l})$ by means of lower and upper bounds. Then, a perturbation expansion around the harmonic approximation $V_H(l)$ discussed in the preceding subsection is used in order to determine the next-to-leading terms.

A lower bound is easily found since

$$E_n > \min_l \{V(l)\} = V(\hat{l}) . \tag{4.31}$$

An upper bound can be obtained from $V_H^{\infty/2}(l)$ as given by (4.28) since $V(l) \leq V_H^{\infty/2}(l)$. This implies

$$E_n < \epsilon_n^{\infty/2} = V(\hat{l}) + \omega(2n + \tfrac{3}{2}) . \tag{4.32}$$

Since $V(\hat{l}) \propto \hat{l}^{-p}$ and $\omega \propto \hat{l}^{-(p+2)/2}$ from (4.11), (4.32) gives $\epsilon_n^{\infty/2} \rightarrow V(\hat{l})$ for $p < 2$. As a consequence,

$$E_n \rightarrow V(\hat{l}) \quad \text{for all } n , \tag{4.33}$$

to leading order. Since the free energy f_s is given by E_0 [see (4.3)], (4.33) already shows that f_s behaves as in MF theory [see (3.3)]. The same conclusion holds for $\hat{l}$.

In order to determine $\xi_{||}$ via (4.7), one has to find the next-to-leading term for E_n since $E_1 - E_0$ vanishes to leading order. This can be obtained from a perturbation expansion of $V(l)$ around the harmonic potential $V_H(l)$ in powers of $\delta V(l)$, where $V_H(l)$ and $\delta V(l)$ have been defined in (4.8) and (4.9). To zeroth order in δV, $E_n = \epsilon_n$, as given by (4.22) and $\psi_n(l) = \varphi_n(l)$ as given by (4.23). To first order in δV, one obtains

$$\begin{aligned} E_n &= \epsilon_n + (\varphi_n \mid \delta V(l) \varphi_n) \\ &= V(\hat{l}) + \omega(n + \tfrac{1}{2})[1 + O((\delta\mu)^z)] , \end{aligned} \tag{4.34}$$

with

$$z = (2-p)/(4+4p) . \tag{4.35}$$

Since $z > 0$ for $p < 2$, (4.34) implies that *both* the leading *and* the next-to-leading term are correctly given by the harmonic approximation. To the same order in δV, the eigenfunctions are

$$\begin{aligned} \psi_n(l) &= \varphi_n(l) + \sum_{k\,(\neq n)} \varphi_k(l) \frac{(\varphi_k \mid \delta V \varphi_n)}{\epsilon_n - \epsilon_k} \\ &= \varphi_n(l) + (\delta\mu)^z \sum_{k\,(\neq n)} A_{nk} \varphi_k(l) , \end{aligned} \tag{4.36}$$

where the exponent z is given by (4.35). The coefficients A_{nk} in (4.36) approach some constant values as $\delta\mu \rightarrow 0$.

From the above results for the eigenvalues E_n and for the eigenfunctions ψ_n, one finds the free energy

$$f_s = E_0 \rightarrow V(\hat{l}) \propto (\delta\mu)^{p/(1+p)} , \tag{4.37}$$

and the three diverging length scales

$$\bar{l} = \frac{\partial E_0}{\partial \delta\mu} \propto (\delta\mu)^{-1/(1+p)} + O((\delta\mu)^{-p/(1+p)}) , \tag{4.38}$$

$$\begin{aligned} \xi_{||} &= (E_1 - E_0)^{-1} = \omega^{-1}[1 + O((\delta\mu)^z)] \\ &\propto (\delta\mu)^{-(2+p)/(2+2p)} , \end{aligned} \tag{4.39}$$

$$\begin{aligned} \xi_\perp &= (2\omega)^{-1/2}[1 + O((\delta\mu)^z)] \\ &\propto (\delta\mu)^{-(2+p)/(4+4p)} . \end{aligned} \tag{4.40}$$

Thus, the MF results (3.3), (3.2), and (3.5) are recovered. To leading order, (4.39) and (4.40) lead to

$$\xi_\perp^2 = \xi_{||}/2 , \tag{4.41}$$

which is identical to the OZ relation (3.11) since $g_0 = \frac{1}{2}$ in $d = 2$ dimensions and $C(0) = \xi_\perp^2$ via (3.13).

Finally, one may obtain an explicit expression for the difference correlation function $\Delta C(x)$ from (4.25) and (4.36):

$$\Delta C(x) = \xi_\perp^2 \left[1 - \sum_{n\,(>0)} \bar{b}_n^{\,2} \exp(-\bar{a}_n x / \xi_{||}) \right] ,$$

with

$$\bar{a}_n = a_n[1 + O((\delta\mu)^z)] ,$$

$$\bar{b}_n = b_n[1 + O((\delta\mu)^z)] ,$$

where a_n, b_n, and z are given by (4.26) and (4.35). To leading order in $\delta\mu$, (4.26) implies $\bar{b}_1 = 1$ and $\bar{b}_n = 0$ for $n \geq 2$. In this limit, $\Delta C(x)$ has the simple form

$$\Delta C(x) = \xi_\perp^2 (1 - e^{-x/\xi_{||}}) . \tag{4.42}$$

For $x \rightarrow 0$ and $x \rightarrow \infty$, $\Delta C(x) \rightarrow 0$ and $\Delta C(x) \rightarrow \xi_\perp^2$, respectively. For $0 \ll x \ll \xi_{||}$, (4.42) implies

$$\Delta C(x) = \tfrac{1}{2} x , \tag{4.43}$$

where (4.41) has been used. This behavior is again identical with the OZ result (3.15) since $\Omega_0 = -\frac{1}{2}$ from (3.13) in $d = 2$ dimensions.

D. Linear potential ($p = \infty$)

For $p > 2$, the harmonic approximation is no longer useful. However, it turns out that another simple approximation can be applied to this case. That approximation is given by the linear potential

$$v(l) = \begin{cases} \infty, & l < 0 \\ \delta\mu\, l, & l > 0. \end{cases} \tag{4.44}$$

This is in fact the short-ranged limit of $V(l)$ as given by (2.24) with $p \rightarrow \infty$. The Schrödinger equation with the potential (4.44) and the boundary condition $\varphi_n(0) = 0$ can be solved exactly in terms of the Airy function $\mathrm{Ai}(x)$.[69,62] The eigenfunctions for (4.44) are

$$\varphi_n(l) = c_n \mathrm{Ai}[(2\delta\mu)^{1/3} l + |\lambda_n|] , \tag{4.45a}$$

with the normalization constant

$$c_n = (2\,\delta\mu)^{1/6} \left[\int_0^\infty dx\, \mathrm{Ai}^2(x + |\lambda_n|) \right]^{-1/2} . \tag{4.45b}$$

The numbers $\lambda_n < 0$ are the zeros of the Airy function: $\mathrm{Ai}(\lambda_n) = 0$. Their numerical values can be found, for instance, in Ref. 69. The eigenvalues ϵ_n for the linear potential (4.44) are

$$\epsilon_n = 2^{-1/3} |\lambda_n| (\delta\mu)^{2/3} . \tag{4.46}$$

Next, consider the difference correlation function $\Delta C(x)$ as defined by (4.6). It is obvious from (4.6) that $\Delta C(x)$ approaches its limiting value $\xi_\perp^2$ exponentially fast for $x \gg \xi_{||} = (E_1 - E_0)^{-1}$. In order to discuss the behavior for $x \ll \xi_{||}$, it is convenient to use the spectral representation of H which gives

$$\begin{aligned} \Delta C(x) &= \xi_\perp^2 - (\varphi_0 \mid l e^{-(H-\epsilon_0)x} l \mid \varphi_0) + \bar{l}^2 \\ &= -\sum_{m=1}^{\infty} \frac{(-x)^m}{m!} (\varphi_0 \mid l (H - \epsilon_0)^m l \mid \varphi_0) . \end{aligned} \tag{4.47}$$

(4.47) holds for any H. For the linear potential considered here,

$$H=-\frac{1}{2}\frac{d^2}{dl^2}+\delta\mu\, l\ ,$$

which implies $[H,l]=-d/dl$ and $[H,[H,l]]=\delta\mu$. Note that $[H,[H,l]]$ commutes with H. As a consequence,

$$[H^m,l]=-2^{m-1}\frac{d}{dl}H^{m-1}+(m-1)2^{m-2}\delta\mu H^{m-2}\ . \tag{4.48}$$

With the help of (4.48), one can calculate all expectation values in (4.47). After some algebra, one finally finds

$$\Delta C(x)=x\overline{\Omega}(x/\xi_{\|})\ , \tag{4.49a}$$

with $\xi_{\|}=(\epsilon_1-\epsilon_0)^{-1}$ and the scaling function

$$\overline{\Omega}(z)=\sum_{m=1}^{\infty}\frac{(-1)^{m+1}}{m!}\gamma_m z^{m-1}\ . \tag{4.49b}$$

The coefficients are independent of $\delta\mu$ and given by

$$\gamma_m=\left[\frac{|\lambda_0|}{|\lambda_1|-|\lambda_0|}\right]^{m-1}\{\tfrac{1}{3}m-\tfrac{1}{12}[(-1)^m-1]\}\ . \tag{4.49c}$$

In the derivation of this expression, the identity $(\varphi_0|(l\,d/dl)\varphi_0)=-\frac{1}{2}$ has been used.

The linear potential $v(l)$ discussed so far is always smaller than the true potential $V(l)$ as given by (2.24). It is also useful to consider the linear potential

$$\overline{v}(l)=\begin{cases}\infty, & l<\overline{l}\\ V(\hat{l})+\delta\mu\, l, & l>\overline{l}\end{cases} \tag{4.50}$$

where the hard wall has been shifted to $l=\hat{l}$. It is easy to see that $\overline{v}(l)\geq V(l)$ for all l. The exact eigenvalues for $\overline{v}(l)$ are

$$\overline{\epsilon}_n=\epsilon_n+V(\hat{l})+\delta\mu\,\hat{l}\ , \tag{4.51}$$

where ϵ_n is given by (4.46). From (3.2) and (3.3), one finds

$$V(\hat{l})+\delta\mu\,\hat{l}\propto(\delta\mu)^{p/(1+p)}\ .$$

As a consequence,

$$\overline{\epsilon}_n\to\epsilon_n,\quad p>2\ . \tag{4.52}$$

E. Fluctuation-dominated regime ($p>2$)

The linear potentials $v(l)$ and $\overline{v}(l)$ considered in the preceding subsection have the property $v(l)\leq V(l)\leq\overline{v}(l)$. As a consequence, the eigenvalues E_n of (4.1) fulfill the inequalities $\epsilon_n\leq E_n\leq\overline{\epsilon}_n$, where ϵ_n and $\overline{\epsilon}_n$ are given by (4.46) and (4.51). It then follows from (4.52) that

$$E_n\to2^{-1/3}|\lambda_n|(\delta\mu)^{2/3},\quad p>2 \tag{4.53}$$

to leading order in $\delta\mu$. Thus, the leading terms of the critical singularities are found to be independent of p for $p>2$.

In order to determine the next-to-leading terms, one may use a quantum-mechanical perturbation expansion of $V(l)$ around $v(l)$ in powers of $W(l+l_0)^{-p}$. To zeroth order, $E_n=\epsilon_n$ as given by (4.46), and $\psi_n(l)=\varphi_n(l)$ as given by (4.45). To first order, one finds

$$\begin{aligned}E_n&=\epsilon_n+(\varphi_n|W(l+l_0)^{-p}\varphi_n)\\&=\epsilon_n[1+O((\delta\mu)^{\overline{z}})]\ ,\end{aligned} \tag{4.54}$$

where the exponent $\overline{z}$ is found to be

$$\overline{z}=\begin{cases}(p-2)/3, & 2<p<3\\ \frac{1}{3}, & 3<p.\end{cases} \tag{4.55}$$

In the same order, the eigenfunctions $\psi_n(l)$ of (4.1) are

$$\begin{aligned}\psi_n(l)&=\varphi_n(l)+\sum_{k\,(\neq n)}\varphi_k(l)\frac{(\varphi_k|W(l+l_0)^{-p}\varphi_n)}{\epsilon_n-\epsilon_k}\\&=\varphi_n(l)+(\delta\mu)^{\overline{z}}\sum_{k\,(\neq n)}B_{nk}\varphi_k(l)\ .\end{aligned} \tag{4.56}$$

The coefficients B_{nk} approach some constant values for $\delta\mu\to0$.

From (4.53)–(4.56), one obtains the following critical behavior. The free energy f_s is given by

$$f_s=2^{-1/3}|\lambda_0|(\delta\mu)^{2/3}[1+O((\delta\mu)^{\overline{z}})]\ , \tag{4.57}$$

where $\lambda_0=-2.338$ is the largest zero of the Airy function Ai(x).[69] The three diverging length scales have the asymptotic behavior

$$\overline{l}=|\lambda_0|(2\delta\mu)^{-1/3}[1+O((\delta\mu)^{\overline{z}})]\ , \tag{4.58}$$

$$\xi_{\|}=2^{1/3}(|\lambda_1|-|\lambda_0|)^{-1}(\delta\mu)^{-2/3}[1+O((\delta\mu)^{\overline{z}})]\ , \tag{4.59}$$

$$\xi_{\perp}=b_0(2\delta\mu)^{-1/3}[1+O((\delta\mu)^{\overline{z}})]\ . \tag{4.60}$$

$|\lambda_1|-|\lambda_0|=2.750$ from Ref. 69, and

$$b_0^2\equiv\int_0^{\infty}dx(x-|\lambda_0|)^2\mathrm{Ai}^2(x-|\lambda_0|)\Big/\int_0^{\infty}dx\,\mathrm{Ai}^2(x-|\lambda_0|)\ .$$

Due to (4.56), the difference correlation function $\Delta C(x)$ is given by (4.49) to leading order in $\delta\mu$. Thus, one finds the scaling form

$$\Delta C(x)=x\overline{\Omega}(x/\xi_{\|})[1+O((\delta\mu)^{\overline{z}})]\ , \tag{4.61}$$

with $\overline{\Omega}(z)$ given by (4.49b). For $0\ll x\ll\xi_{\|}$, leads to

$$\Delta C(x)=\gamma_1 x=\tfrac{1}{2}x\ , \tag{4.62}$$

where (4.49c) has been used for $m=1$. Note that exactly the same behavior for $\Delta C(x)$ was obtained in the MF regime with $p<2$; see (4.43). As a consequence, $\Delta C(x)=\frac{1}{2}x$ for $0\ll x\ll\xi_{\|}$ in $d=2$ dimensions, *both* in the fluctuation-dominated regime *and* in the MF regime.

F. The marginal case ($p=2$)

For $p=2$, the perturbation expansions used on Secs. IV C and IV E break down. This is obvious from (4.36) and (4.56) since the correction exponents z and $\bar{z}$ as given by (4.35) and (4.55) vanish for $p=2$. On the other hand, the lower and upper bounds derived from the harmonic and the linear potentials still hold. Thus,

$$V(\hat{l})\leq E_n \leq V(\hat{l})+\omega(2n+\tfrac{3}{2}) \tag{4.63}$$

from (4.31) and (4.32), and

$$\epsilon_n \leq E_n \leq \epsilon_n + V(\hat{l})+\delta\mu\,\hat{l} \tag{4.64}$$

from (4.46) and (4.57). Since $\epsilon_n \propto V(\hat{l}) \propto \omega \propto (\delta\mu)^{2/3}$ for $p=2$, these inequalities imply

$$E_n \rightarrow A_n(\delta\mu)^{2/3}, \quad p=2 \,. \tag{4.65}$$

As a consequence, the free energy is

$$f_s = E_0 \propto (\delta\mu)^{2/3} \,, \tag{4.66}$$

and the mean value of the interfacial distance is

$$\bar{l}=\frac{\partial E_0}{\partial \delta\mu} \propto (\delta\mu)^{-1/3} \tag{4.67}$$

to leading order in $\delta\mu$ also for $p=2$.

If the amplitudes $A_0 \neq A_1$ in (4.65), it follows that

$$\xi_{\|}=(E_1-E_0)^{-1} \propto (\delta\mu)^{-2/3} \,. \tag{4.68}$$

In fact, (4.64) implies that $A_0 < A_1$ for sufficiently small Hamaker constant W since $V(\hat{l})+\delta\mu\,\hat{l} \propto W^{1/3}$, which leads to

$$\epsilon_0 + V(\hat{l})+\delta\mu\,\hat{l} < \epsilon_1$$

for small W. On the other hand, if A_0 and A_1 were equal, it would follow that $\xi_{\|} \propto (\delta\mu)^{-\nu_{\|}}$ with $\nu_{\|} > \frac{2}{3}$. This is not to be expected since $\xi_{\|} \propto (\delta\mu)^{-2/3}$ for $p>2$ and $\xi_{\|} \propto (\delta\mu)^{-(2+p)/(2+2p)}$ for $p<2$, which goes to $(\delta\mu)^{-2/3}$ as $p \rightarrow 2$ from below. Thus, I conclude that (4.68) holds for arbitrary values of W.

The behavior of the interfacial roughness

$$\xi_{\perp}^2 = (\psi_0 \,|\, (l-\bar{l})^2 \psi_0) \tag{4.69}$$

can be obtained from an asymptotic analysis for the ground-state eigenfunction $\psi_0(l)$ of (4.1). For large $l \gg \hat{l}$, the potential $V(l)$ is dominated by the linear term $\delta\mu\, l$. This leads to

$$\psi_0(l) \propto \exp(-\beta l^{3/2}) \,,$$

with $\beta \equiv \frac{2}{3}(2\,\delta\mu)^{1/2}$. For $l_0 \ll l \ll \hat{l}$, on the other hand, the potential $V(l)$ can be approximated by Wl^{-2}. This implies

$$\psi_0(l) \propto l^q \,,$$

with

$$q \equiv \tfrac{1}{2}[1+(1+4W)^{1/2}] \,.$$

If one matches both asymptotic expressions at $l=\hat{l}$, one finds

$$\psi_0(l) \propto \begin{cases} l^q, & l<\hat{l} \\ \hat{l}^q \exp(-\beta l^{3/2}), & l>\hat{l} \end{cases} \tag{4.70}$$

since

$$\beta \hat{l}^{\,3/2} \propto (\delta\mu)^{1/2}(\delta\mu)^{-1/2} = O(1) \,.$$

From (4.70) and (4.69), it follows that

$$\xi_{\perp} \propto \hat{l} \propto (\delta\mu)^{-1/3}, \quad p=2 \,. \tag{4.71}$$

V. TWO DIFFERENT SCALING REGIMES

In the two foregoing sections, a variety of critical exponents have been calculated in MF theory and for $d=2$. Let us summarize what has been found to leading order in $\delta\mu$. First, the free energy f_s has the asymptotic behavior

$$f_s \propto (\delta\mu)^{2-\alpha_s} \,, \tag{5.1}$$

with

$$\alpha_s = \begin{cases} (2+p)/(1+p), & \text{MF}; p<2 \text{ and } d=2 \\ \frac{4}{3}, & p \geq 2 \text{ and } d=2 \end{cases} \tag{5.2}$$

from (3.3), (4.37), (4.57), and (4.66). Note that the corresponding specific heat $c_s = \partial^2 f_s / \partial\,\delta\mu^2 \propto (\delta\mu)^{-\alpha_s}$, which motivates the exponent notation.

The mean thickness $\bar{l}$ of the wetting layer was found to diverge as

$$\bar{l} \propto (\delta\mu)^{\beta_s} \,, \tag{5.3}$$

$$\beta_s = \begin{cases} -1/(1+p), & \text{MF}; p<2 \text{ and } d=2 \\ -\frac{1}{3}, & p \geq 2 \text{ and } d=2 \end{cases} \tag{5.4}$$

from (3.2), (4.38), (4.58), and (4.67). The correlation length

$$\xi_{\|} \propto (\delta\mu)^{-\nu_{\|}} \,, \tag{5.5}$$

with

$$\nu_{\|} = \begin{cases} (2+p)/(2+2p), & \text{MF}; p<2 \text{ and } d=2 \\ \frac{2}{3}, & p \geq 2 \text{ and } d=2 \end{cases} \tag{5.6}$$

from (3.5), (4.39), (4.59), and (4.68), and the interfacial roughness

$$\xi_{\perp} \propto (\delta\mu)^{-\nu_{\perp}} \,, \tag{5.7}$$

with

$$\nu_{\perp} = \begin{cases} 0(\log), & \text{MF}, d=3 \\ (3-d)(2+p)/(4+4p), & \text{MF}, d<3 \\ (2+p)/(4+4p), & p<2, d=2 \\ \frac{1}{3}, & p \geq 2, d=2 \end{cases} \tag{5.8}$$

from (3.13), (3.10), (4.40), (4.60), and (4.71). Note that $\nu_{\perp}$ depends already on d in MF theory.

In addition, the correlation function $C(x)$ of the interfacial fluctuations has been calculated both within OZ theory and in $d=2$. For $d>3$, OZ theory yields the scaling form

$$C(x)=x^{3-d}\Omega(x/\xi_{\parallel}) , \tag{5.9}$$

where $\Omega(y)$ is given by (3.8). For $d\leq 3$, it is more convenient to consider the difference correlation function $\Delta C(x)\equiv C(0)-C(x)$. OZ theory gives

$$\begin{aligned}\Delta C(x)&=x^{3-d}\overline{\Omega}(x/\xi_{\parallel})\\&=\xi_{\perp}^{2}[1-\overline{g}(x/\xi_{\parallel})] ;\end{aligned} \tag{5.10}$$

see (3.15). The same scaling form for $\Delta C(x)$ is found in $d=2$ dimensions to leading order in $\delta\mu$ both for $p<2$ and for $p>2$; see (4.42) and (4.61). For intermediate x values, i.e., for $0\ll x\ll\xi_{\parallel}$,

$$C(x)=\Omega_0 x^{-(d-3)}, \quad \text{OZ}, \ d>3 \tag{5.11}$$

from (3.17), and

$$\Delta C(x)=\begin{cases}(1/4\pi)\ln(x), & \text{OZ}, \ d=3\\ |\Omega_0|\, x^{3-d}, & \text{OZ}, \ d<3\\ \frac{1}{2}x, & d=2\end{cases} \tag{5.12}$$

from (3.18), (3.19), (4.43), and (4.62).

If one defines the critical exponent η in the usual way by

$$\begin{aligned}C(x) &\propto x^{-(d-3+\eta)} ,\\ \Delta C(x) &\propto x^{-(d-3+\eta)} ,\end{aligned} \tag{5.13}$$

for $0\ll x\ll\xi_{\parallel}$, (5.11) and (5.12) imply

$$\eta=0 \quad \text{for all } d . \tag{5.14}$$

Thus, the interface coordinate $l(x)$ has no anomalous dimension. This is also true for a fluctuating interface in a weak gravitational field.[57] In the latter case, the effective interface potential $V(l)\propto l^2$, i.e., the field theory for l is a Gaussian model, and, thus, $\eta=0$ is to be expected. On the other hand, the results obtained above show that *$\eta=0$ holds even for interface potentials which are strongly non-Gaussian.*

The critical exponents α_s, β_s, $\nu_{\parallel}$, $\nu_{\perp}$, and η are not independent. First of all, β_s is related to α_s by thermodynamics since $\overline{l}\propto$ adsorption $\equiv\partial f_s/\partial\delta\mu$. As a consequence,

$$\beta_s=1-\alpha_s . \tag{5.15}$$

This scaling relation has been obtained before for different types of wetting transitions.[19] Next, the length scales $\xi_{\perp}$ and $\xi_{\parallel}$ are related by

$$\xi_{\perp}=\xi_{\parallel}^{(3-d)/2}, \quad d\leq 3 . \tag{5.16}$$

This holds both in OZ theory—see (3.13) and (3.11)—and in $d=2$ dimensions for all values of p—see (4.41) and (4.59), and (4.60). As a consequence, one has the scaling relation[33,45]

$$\nu_{\perp}=\tfrac{1}{2}(3-d)\nu_{\parallel} . \tag{5.17}$$

This relation is intimately related to the identity $\eta=0$. Assume, for a moment, that η were not equal to zero. As a consequence, $\Delta C(x)$ would have the more general scaling form

$$\Delta C(x)=x^{-(d-3+\eta)}\overline{\Omega}(x/\xi_{\parallel}) ,$$

and, thus, $\Delta C(x)\rightarrow\xi_{\parallel}^{-(d-3+\eta)}$ for large x. On the other hand, $\Delta C(\infty)=C(0)=\xi_{\perp}^{2}$ by definition, which leads to $\nu_{\perp}=\frac{1}{2}(3-d-\eta)\nu_{\parallel}$. Thus, the scaling relation (5.17) implies that $\eta=0$. The same scaling relation has been found previously for critical wetting transitions[33] and for wetting by critical layers.[70] Thus, $\eta=0$ holds also for those transitions.

Additional scaling relations follow from hyperscaling arguments. In order to determine the upper critical dimension (UCD) $d^*(p)$, one may employ the Ginzburg criterion $f_s\sim\xi_{\parallel}^{-(d-1)}$ where both quantities are calculated within MF theory. This leads to[18]

$$d^*(p)=(3p+2)/(p+2) . \tag{5.18}$$

For $d\leq d^*(p)$, the hyperscaling relation

$$2-\alpha_s=(d-1)\nu_{\parallel} \tag{5.19}$$

should hold. Equation (5.19) is indeed valid in $d=2$ dimensions for $p\geq 2$; see (5.2) and (5.6). The UCD (5.18) can also be obtained from the "contact relation"[43]

$$\xi_{\perp}\sim\hat{l} . \tag{5.20}$$

This relation is also valid for $d=2$ and $p\geq 2$, i.e., in the fluctuation-dominated regime; see (5.3) and (5.7). Since (5.20) holds both in $d=d^*(p)$ and for those p values with $d^*(p)>2$, it is reasonable to assume that (5.20) holds for all $d\leq d^*(p)$. This implies the additional scaling relation

$$\nu_{\perp}=-\beta_s, \quad d\leq d^*(p) . \tag{5.21}$$

There is one exceptional case where $\nu_{\perp}=-\beta_s$ although $\xi_{\perp}\ll\overline{l}$. This happens for short-range forces ($p=\infty$) in $d=3$ dimensions. In this case, $\overline{l}\propto\ln(1/\delta\mu)$ and $\xi_{\perp}\propto[\ln(1/\delta\mu)]^{1/2}$ from (3.11). Thus, $\nu_{\perp}=-\beta_s=0$. This case is exceptional since the UCD $d^*(p=\infty)$ for wetting coincides with the UCD $d^{**}=3$ for roughening.

If one combines the four scaling relations (5.15), (5.17), (5.19), and (5.21), one finds that the critical exponents may be expressed as explicit functions of d. As a result, one finds

$$\alpha_s=4/(d+1) , \tag{5.22}$$

$$\nu_{\parallel}=2/(d+1) , \tag{5.23}$$

$$\nu_{\perp}=-\beta_s=(3-d)/(d+1) , \tag{5.24}$$

for $d\leq d^*(p)$.[71] The expression (5.23) for $\nu_{\parallel}$ can also be obtained in two alternative ways. First, one may use renormalization-group arguments to show that the scaling index $y_{\delta\mu}$ of the scaling field $\delta\mu$ is given by $y_{\delta\mu}=(d+1)/2$ if l has no anomalous dimension. Equation (5.23) is recovered from $\nu_{\parallel}=1/y_{\delta\mu}$. In addition, one may give a heuristic argument similar to those used by Fisher in Ref. 53. Consider an interfacial fluctuation in the form of a droplet with "volume" $\xi_{\perp}\xi_{\parallel}^{d-1}$. The energy of this droplet is given by $\delta\mu\,\xi_{\perp}\xi_{\parallel}^{d-1}$. Such fluctuations are likely to occur if

$$\delta\mu\,\xi_\perp\xi_\parallel^{d-1} \sim k_BT \sim \text{const} . \tag{5.25}$$

It then follows from (5.5) and (5.16) that $\nu_\parallel = 2/(d+1)$.

For $d \geq d^*(p)$, MF theory should apply. In this case, α_s, β_s, and $\nu_\parallel$ are independent of d and have the same value as in $d = d^*(p)$:

$$\alpha_s = 4/[d^*(p)+1] , \tag{5.26}$$

$$\nu_\parallel = 2/[d^*(p)+1] , \tag{5.27}$$

$$\beta_s = [d^*(p)-3]/[d^*(p)+1] . \tag{5.28}$$

The exponent $\nu_\perp$ is somewhat special since it depends on d even in MF theory; see (5.8). From (5.22)–(5.28), one can deduce two additional scaling laws which hold *both* for $d > d^*(p)$ *and* for $d < d^*(p)$:

$$\alpha_s = 2\nu_\parallel , \tag{5.29}$$

$$\beta_s = 1 - 2\nu_\parallel . \tag{5.30}$$

In fact, these relations are also valid at critical wetting transitions,[19] and for wetting by critical layers.[70]

In summary, there are two different scaling regimes for complete wetting. In the *fluctuation-dominated regime* below the UCD $d^*(p)$ as given by (5.18), the interfacial fluctuations are so strong that the two interfaces have frequent contacts. This situation is shown schematically in Fig. 4(a). In this case, the fluctuating interface probes the whole region between $l=0$ and $l=\bar{l}$. As a consequence, the repulsive l^{-p} term of the effective interface potential plays no role for the leading singularities of the critical behavior, and the critical exponents are independent of p. In the *MF regime*, on the other hand, above the UCD $d^*(p)$, the interface fluctuations are confined to a small fraction of the mean distance $\bar{l}$ between the interfaces, i.e., $\bar{l} \gg \xi_\perp$ as shown schematically in Fig. 4(b). In this case, the l^{-p} term determines $\bar{l}$, and the critical exponents depend on p.

VI. EXPERIMENTS

The approach towards complete wetting has already been observed in three-dimensional systems. Two such systems have been investigated, namely adsorbed liquid layers[1–8] and gravity-thinned layers in binary mixtures.[9–14] In both cases, the underlying microscopic interactions are dispersion or van der Waals forces. As long as retardation effects can be ignored, these forces have an attractive long-ranged tail as given by (2.21) with $q=6$.[15,16] For sufficiently large separations of the molecules, retardation effects become important, and these forces are described by (2.21) with $q=7$.[16,60] The length scale for the crossover from the nonretarded to the retarded form of the van der Waals forces is given by the characteristic absorption wavelength of the particles,[72] and is typically $< 10^{-5}$ cm. This crossover has been experimentally studied by direct measurement of the van der Waals forces between two glass surfaces[72] (see also Ref. 2).

For interactions with $q=6$ or $q=7$, one has an effective interface potential $V(l) \propto l^{-p}$ with $p=2$ or $p=3$ in $d=3$; see (2.22). It follows from (5.18) that the corresponding upper critical dimensions $d^*(p=2)=2$ and $d^*(p=3)=\frac{11}{5}$ are both smaller than $d=3$. As a consequence, these systems should be correctly described by MF theory as given by Sec. III above.

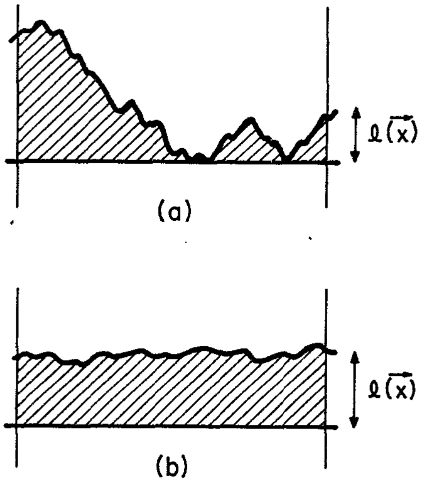

FIG. 4. Typical interfacial configurations (a) in the fluctuation-dominated regime where the two interfaces which bound the wetting layer meet frequently, and (b) in the mean-field regime where the mean distance between these interfaces is much larger than their roughness.

A. Adsorbed layers

In this case, the effective interface potential $V(l)$ is given by (2.2), and the mean thickness of the wetting layer is

$$\bar{l} = \left[\frac{\delta\mu}{2W}\right]^{\beta_s} \propto (\mu^* - \mu)^{\beta_s} , \tag{6.1}$$

with

$$\beta_s = \begin{cases} -\frac{1}{3}, & \text{nonretarded} \\ -\frac{1}{4}, & \text{retarded.} \end{cases} \tag{6.2}$$

$\delta\mu$ and W are given by (2.4) and (2.5). Note that both W and $\delta\mu$ contain a factor $(\rho_L - \rho_V)$, which drops out in (6.1). This cancellation occurs for any type of interaction, as can be seen from the expression (2.23) for the generalized Hamaker constant. Note that the interface potential $V(l)$ is expected to be proportional to $(\rho_L - \rho_V)$ since it must vanish as soon as both phases L and V become identical.

The chemical potential difference $\mu^* - \mu$ is not easily controlled in an experiment. However, $\mu^* - \mu$ may be expressed in terms of the vapor pressure P and the temperature T. If the vapor is treated as an ideal gas of classical particles, one has[73]

$$\mu^* - \mu = k_BT \ln(P^*/P) \tag{6.3}$$

for an isothermic approach towards the liquid-vapor coexistence curve given by $P = P^*(T)$. For an isobaric approach towards coexistence,

$$\mu^* - \mu = k_B T^* g(P) t + O(t^2) , \tag{6.4a}$$

with $t \equiv (T^* - T)/T^*$, where the coexistence curve is described by $T = T^*(P)$. The prefactor $g(P)$ is given by[73]

$$g(P) = \ln[\zeta (k_B T^*)^{c_p} / P] - c_p , \tag{6.4b}$$

where c_p is the classical specific heat, and ζ is related to the chemical constant of the vapor. For a monoatomic gas, $c_p = \frac{5}{2}$ and $\zeta = (2\pi h^2/m)^{-3/2}$.

In the experimental work of Refs. 1–3, 5, 7, and 8, β_s has been measured along an isothermic approach towards coexistence. In Refs. 1, 2, 5, and 8, $|\beta_s| \simeq \frac{1}{3}$ has been found, in agreement with the theoretical prediction (6.2) for nonretarded van der Waals forces. In Ref. 3, a value $|\beta_s| \simeq \frac{1}{2}$ was obtained from the adsorption isotherms for ether and methanol adsorbed on gold. In Ref. 7, $|\beta_s| \simeq \frac{2}{5}$ has been found for adsorption of propane on graphite. Thus, a value $|\beta_s| > \frac{1}{3}$ has been extracted from these experiments, which means that the thickness of the wetting layer seems to grow faster than expected from (6.1).[74] In the latter experiment, where the substrate consisted of graphite, strong finite-size effects in the form of capillary condensation could explain this discrepancy. However, this explanation does not apply to the experiments of Ref. 3 where the substrate consisted of gold. In this case, some attempts have been made in the literature to relate the apparent exponent $|\beta_s| > \frac{1}{3}$ to the heterogeneity of the polycrystalline substrate[15] and to the finite thickness of the liquid-vapor interface.[75] The largest values for $\bar{l}$ which have been obtained in the adsorption experiments just described were 60–70 layers or 200–300 Å.[3,8] Thus, the range of $\bar{l}$ values which seems accessible to present experimental techniques is

$$10^{-7} \lesssim \bar{l} \lesssim 10^{-5}\ \text{cm} . \tag{6.5}$$

The experimental work done so far has been devoted to the measurement of the thickness $\bar{l}$ of the wetting layer. Another quantity of great interest would be the correlation length $\xi_{\parallel}$. Within MF theory, which is applicable here, $\xi_{\parallel}$ is given by (3.4c). For nonretarded van der Waals force ($p = 2$), (3.4c) leads to

$$\xi_{\parallel} = \left[\frac{\sigma}{6W} \right]^{1/2} \bar{l}^2 \propto (\mu^* - \mu)^{-2/3} . \tag{6.6}$$

For $\sigma \sim 10$ ergs/cm^2 and $W \sim 10^{-14}$ erg, (6.6) gives

$$\xi_{\parallel} \approx (10^7\ \text{cm}^{-1}) \bar{l}^2 . \tag{6.7}$$

Thus for the accessible range of $\bar{l}$ values given by (6.5) one finds that

$$10^{-7} \lesssim \xi_{\parallel} \lesssim 10^{-3}\ \text{cm} . \tag{6.8}$$

Of course, this is only a crude estimate. It can, however, be easily improved if one inserts more precise values for σ and W into (6.6). For $\bar{l} \approx 10^{-5}$ cm, retardation effects would become important which lead to $\xi_{\parallel} \propto (\mu^* - \mu)^{-5/8}$; see (3.5) with $p = 3$.

One way to observe $\xi_{\parallel}$ *is via small-angle scattering* of light from the liquid-vapor interface which bounds the wetting layer. This technique has already been used to study the capillary waves on a free liquid-vapor interface.[76–78] In these experiments, the diffuse scattering of light around the reflected beam has been measured. In the plane of incidence, the intensity of the diffuse scattering is given by[77]

$$\frac{dI}{d\Omega} = (\text{area}) \times I_R M C(q) , \tag{6.9}$$

where I_R is the intensity of the reflected beam, and

$$C(q) = \int \frac{d^2 q}{(2\pi)^2} e^{i\mathbf{q}\cdot\mathbf{x}} \langle [l(\mathbf{x}) - \bar{l}][l(0) - \bar{l}] \rangle \tag{6.10}$$

is the Fourier transform of the correlation function for the interfacial fluctuations. The factor M in (6.9) depends on the scattering geometry and is given by $M = k_0^4 \cos^3\theta / (4\pi^2)$, where k_0 and θ are the wave number of the incident beam and the reflection angle; see Ref. 77. The formula (6.9) holds for the diffuse scattering from *any fluctuating interface. Near wetting in* $d = 3$ *dimen*sions, the correlation function $C(q)$ is given by (3.6):

$$C(q) = \frac{k_B T}{\sigma_{LV}} \frac{1}{q^2 + \xi_{\parallel}^{-2} + \kappa^{-2}} . \tag{6.11}$$

The additional term $\sigma_{LV} \kappa^{-2} = \partial^2 V_g(l) / \partial l^2$ due to gravity where $V_g(l)$ is given by (2.12) has been included in (6.11) for the sake of completeness. However, for the range of accessible $\xi_{\parallel}$ values given by (6.8), $\xi_{\parallel}$ is much smaller than the capillary length $\kappa \approx 10^{-1}$ cm, which means that the κ^{-2} term in (6.1) can be neglected. Thus, near complete wetting, the intensity of the diffuse scattering is given by

$$\frac{dI}{d\Omega} \propto \frac{k_B T}{\sigma_{LV}} \frac{1}{q^2 + \xi_{\parallel}^{-2}} . \tag{6.12}$$

The small-angle scattering just described measures the spatial distribution of the interface fluctuations. Another interesting experiment would consist in the measurement of the dispersion relation for the capillary waves. The theoretical prediction for this relation is derived in Sec. VI C below.

For three-dimensional systems, the interfacial roughness can hardly be observed since it is only logarithmically divergent; see (3.13) and (3.11). For two-dimensional systems, on the other hand, $\xi_{\perp}$ diverges as a power law, i.e., $\xi_{\perp} \propto (\mu^* - \mu)^{-\nu_1}$; see (5.7) and (5.8). This applies even to wetting by two-dimensional "solids" since the roughening temperature T_R is zero in $d = 2$ dimensions. Consider, for instance, the one-dimensional interface which separates two (almost) coexisting phases *within* an adsorbed monolayer. If the adsorbed particles interact via van der Waals forces, the effective interface potential contains a term $W l^{-3}$ for nonretarded and a term $W l^{-4}$ for retarded forces; see (2.22). Such systems would probe the fluctuation-dominated regime since the UCD $d^*(p = 3)$ and $d^*(p = 4)$ are both larger than $d = 2$. As a consequence, one would have

$$\bar{l} \propto \xi_{\perp} \propto (\delta\mu)^{-1/3}, \quad d = 2 \tag{6.13}$$

both for retarded and for nonretarded forces. These length scales should show up in the diffuse scattering of x rays as has been argued elsewhere.[33,79] It has also been conjectured[33,79] that the behavior (6.13) has already been observed at the freezing transition of Xe on graphite.[80]

B. Gravity-thinned layers in binary mixtures

As discussed in Sec. II B, two types of gravity-thinned layers have been experimentally explored. One type of layer [see Fig. 2(a)] is bounded by a liquid-vapor and a liquid-liquid interface. In the absence of gravity, the B phase would completely wet the vapor. As a consequence, the interfacial tensions satisfy $\sigma_{VA} = \sigma_{VB} + \sigma_{AB}$,[54] where the subscripts refer to vapor, A phase, and B phase. Similarly, one has $\sigma_{SB} = \sigma_{SA} + \sigma_{AB}$ for the other type of gravity-thinned layer [see Fig. 2(c)]. These equalities are most likely to hold if σ_{AB} is small. For this reason, most experiments have been performed near the consolute point of the binary mixture where σ_{AB} goes to zero. From a theoretical point of view, this is a major complication since the bulk correlation length ξ_b may become comparable to or even larger than the thickness $\bar{l}$ of the wetting layer. As has been emphasized in Sec. II, the theory described here is only applicable as long as $\xi_b \ll \bar{l}$. In the following, this is always tacitly assumed. For $\xi_b \simeq \bar{l}$, one expects crossover effects between wetting and bulk critical phenomena. The present understanding of those effects has been discussed in the recent review by Sullivan and Telo da Gama.[27]

For gravity-thinned layers, the effective interface potential $V(l)$ is given by (2.13) or (2.16). Since MF theory is valid here, the thickness of the wetting layer is

$$\bar{l} = \left[\frac{\delta\mu}{2W} \right]^{\beta_s} \propto \left[\frac{\bar{\rho}_B - \bar{\rho}_A}{\rho_A - \rho_B} \right]^{\beta_s} L^{\beta_s} , \tag{6.14}$$

with $\beta_s = -\frac{1}{3}$ for nonretarded and $\beta_s = -\frac{1}{4}$ for retarded van der Waals forces just as in (6.2). Throughout this section, the variable $L = L_A$ or L_B denotes the thickness of the intermediate liquid phase; see Figs. 2(a) and 2(c). In (6.14), the approximate expressions (2.15) and (2.16b) for the Hamaker constant W has been used.

In order to have a gravity-thinned layer, the mass densities must satisfy $\bar{\rho}_A < \bar{\rho}_B$. On the other hand, (2.15) and (2.16b) imply that the particle number densities must fulfill $\rho_A > \rho_B$ in order to have $W > 0$.[81] It is convenient to express these inequalities in terms of the mass densities $\bar{\rho}_1$ and $\bar{\rho}_2$ of the pure liquids 1 and 2. To be specific, let us assume that the A phase consists mainly of liquid 1. It is easy to show that, for a pure mixture, the inequalities $\bar{\rho}_A < \bar{\rho}_B$ and $\rho_A > \rho_B$ are equivalent to

$$\bar{\rho}_1 < \bar{\rho}_2 , \tag{6.15a}$$

$$\bar{\rho}_1 > (m_1/m_2)\bar{\rho}_2 , \tag{6.15b}$$

irrespective of the mole fractions for the two liquid phases if one neglects the volume change on mixing. m_1 and m_2 are the masses of the molecules in liquid 1 and 2, respectively. It seems that (6.15) indeed holds for most of those binary mixtures where a reproducible wetting layer has been absorbed. In particular, it holds for the pairs methylcyclohexane/perfluoromethyl-cyclohexane, isopropanol/perfluoromethyl-cyclohexane, and nitromethane/carbondisulfite, which have been studied in Refs. 10, 12, and 14.

One mixture for which the inequality (6.15b) is violated is methanol-cyclohexane. For this mixture, strong nonequilibrium effects have been reported.[11,12] No wetting layer present in thermal equilibrium has been found. Since $\bar{\rho}_1 < (m_1/m_2)\bar{\rho}_2$ implies $\rho_A < \rho_B$, one finds $W < 0$ from (2.15), i.e., the interfaces are attracted rather than repelled by the Wl^{-2} term. Thus, one might speculate that the nonexistence of a wetting layer in methanol-cyclohexane is due to a negative Hamaker constant W. From a theoretical point of view, $W < 0$ implies that one has to determine the next-to-leading terms of the interface potential $V(l)$.[39–43] Whatever l dependence the leading correction term might have, it certainly leads to a much smaller value for the thickness $\bar{l}$ than one would find for the case $W > 0$. It has also been observed that a wetting layer appears in the methanol-cyclohexane mixture if one adds a small amount of water to it.[11,82] This would happen if W became positive for the less pure mixture. More generally, one would expect that the sign of the Hamaker constant W could be tuned in binary mixtures by the addition of impurities. In particular, one might be able to obtain $W = 0$ in this manner, which corresponds to *critical* wetting. Note that, for gravity-thinned layers, critical wetting would mainly show up in a changed L dependence of $\bar{l}$.

Let us now focus on those mixtures for which a stable wetting layer has already been observed. For the *V-B-A* geometry [see Fig. 2(a)], wetting layers with a thickness $\bar{l}$ up to ~800 Å have been found.[10] For the *S-A-B* geometry [see Fig. 2(c)], on the other hand, a much larger thickness $\bar{l} \sim 6000$ Å was observed.[14] Thus, the accessible range of $\bar{l}$ values for gravity thinned layers seems to be

$$10^{-7} \lesssim \bar{l} \lesssim 10^{-4} \text{ cm} . \tag{6.16}$$

Note that crossover length for retardation effects is expected to be $\lesssim 800$ Å, which lies well inside this range of $\bar{l}$. Thus, one should be able to observe this crossover. In particular, it should be possible to measure the $L^{-1/4}$ dependence predicted by (6.14) for retarded van der Waals forces.

In the above experiments, the thickness L of the intermediate liquid phase was typically

$$10^{-1} \lesssim L \lesssim 10 \text{ cm} . \tag{6.17}$$

Strictly speaking, these L values should be regarded as the *mean* values $\bar{L}$ for the distance between the two *A-B* interfaces [see Figs. 2(a) and 2(c)]. For general interfacial configurations, L will also fluctuate: $L(\mathbf{x}) = \bar{L} + \delta L(\mathbf{x})$. To be specific, consider the *S-A-B* geometry shown in Fig. 2(c). One may estimate the magnitude of δL by considering two extreme cases for the behavior of the upper *A*-*B* interface. First, assume that this interface does not fluctuate at all. As a consequence, the variation δL is only due to the fluctuations of the lower *A*-*B* interface: $\delta L(\mathbf{x})=l(\mathbf{x})-\bar{l}\equiv\delta(\mathbf{x})$. The typical values for δ are given by the interfacial roughness $\xi_\perp$. In the present context,

$$\xi_\perp=\left[\frac{k_BT}{\sigma_{AB}}\ln(\xi_\parallel/a)\right]^{1/2} \tag{6.18}$$

from (3.7) and (3.11), where a is some microscopic length scale. For an interfacial tension $\sigma_{AB}\sim 1$ erg/cm^2, (6.18) leads to $\xi_\perp\sim 10^{-7}$ cm. On the other hand, one may consider the situation where the upper *A*-*B* interface fluctuates independently from the lower case. Such fluctuations are governed by gravity. They lead to a roughness

$$\bar{\xi}_\perp=\left[\frac{k_BT}{\sigma_{AB}}\ln(\kappa_{AB}/a)\right]^{1/2} \tag{6.19}$$

for the upper *A*-*B* interface, where κ_{AB} is its capillary length. Since $\bar{\xi}_\perp$ is comparable to $\xi_\perp$ as given by (6.18), these two extreme types of behavior lead to the estimates $\delta L\lesssim 10^{-7}$ cm, and

$$10^{-6}\lesssim\delta L/L\lesssim 10^{-8}$$

for the range of L values given by (6.17). As a consequence, one may ignore the fluctuations of L, and replace L by its mean value. This was the second assumption made at the beginning of Sec. II B.

As in the case of adsorbed layers, the experiments done so far have focused on the thickness $\bar{l}$ of the gravity-thinned layers. It would again be very interesting to investigate the correlation length $\xi_\parallel$. The theory described here predicts the behavior

$$\xi_\parallel=\left[\frac{\sigma}{6W}\right]^{1/2}\bar{l}^{(p+2)/2}\,, \tag{6.20}$$

with $p=2$ and $p=3$ for nonretarded and retarded van der Waals forces. The interfacial tension $\sigma=\sigma_{AB}$ for the *S*-*A*-*B* geometry [see Fig. 2(c)], and $\sigma=\sigma_{AB}\sigma_{BV}/(\sigma_{AB}+\sigma_{BV})$ for the *V*-*B*-*A* geometry [see Fig. 2(a)]. The Hamaker constant W is given by (2.14)–(2.16). If one inserts (6.14) and (6.20), one finds

$$\xi_\parallel\propto L^{-\nu_\parallel}\,, \tag{6.21a}$$

$$\nu_\parallel=\begin{cases}\frac{2}{3}, & \text{nonretarded}\\ \frac{5}{8}, & \text{retarded.}\end{cases} \tag{6.21b}$$

The prefactor $(\sigma/W)^{1/2}$ in (6.20) vanishes at the bulk critical temperature T_c of the consolute point. Since $\sigma\propto\tau^\mu$ and $W\propto\tau^\beta$, with $\tau=(T_c-T)/T_c$, one has $(\sigma/W)^{1/2}\propto\tau^{(\mu-\beta)/2}$, where the bulk critical exponents μ and β are $\mu\simeq\frac{5}{4}$ and $\beta\simeq\frac{1}{3}$. This leads to the estimate

$$\xi_\parallel\sim(10^7\text{ cm}^{-1})\times\tau^{(\mu-\beta)/2}\bar{l}^{(p+2)/2}\,, \tag{6.22}$$

in analogy to the estimate (6.7).

The length scale $\xi_\parallel$ may again be measured by small-angle scattering of light as discussed in Sec. IV A. First, consider the case of an *S*-*A*-*B* layer. Since its geometry is identical to the one for adsorbed layers, the scattering intensity is again given by the formulas (6.9)–(6.12), where σ_{LV} has to be replaced by σ_{AB}. For the *V*-*B*-*A* layer, on the other hand, one would typically scatter from the *B*-*V* interface described by the interface coordinate $l_1(\mathbf{x})$ [see Figs. 2(a) and 2(b)]. In this case, one will find a diffuse scattering intensity

$$\frac{dI}{d\Omega}\propto C_1(q)\,, \tag{6.23}$$

with

$$C_1(q)=\int\frac{d^2q}{(2\pi)^2}e^{i\mathbf{q}\cdot\mathbf{x}}\langle l_1(\mathbf{x})l_1(\mathbf{0})\rangle\,, \tag{6.24}$$

where the definition $\bar{l}_1\equiv\langle l_1\rangle\equiv 0$ has been used. This correlation function can be expressed as the sum of two Lorentzians, as will be shown next.

First, let us go back to the free energy (2.17) for the two fluid-fluid interfaces described by $l_1(\mathbf{x})$ and $l_2(\mathbf{x})$. In the MF regime, considered here, the interface potential $V(l)=V(l_2-l_1)$ may be replaced by the harmonic potential $\frac{1}{2}\sigma\xi_\parallel^{-2}(l-\bar{l})^2$. This leads to the Gaussian model

$$\begin{aligned}F\{l_1,l_2\}=\int d^2x[\,&\tfrac{1}{2}\sigma_1(\nabla l_1)^2+\tfrac{1}{2}\sigma_2(\nabla l_2)^2\\&+\tfrac{1}{2}\sigma\xi_\parallel^{-2}(l_2-\bar{l}_2-l_1)^2+\tfrac{1}{2}\sigma_1\kappa_1^{-2}l_1^2]\,,\end{aligned} \tag{6.25}$$

where the additional term (2.20) due to gravity has also been included. As before, $\sigma_1\equiv\sigma_{BV}$, $\sigma_2=\sigma_{AB}$, $\sigma=\sigma_1\sigma_2/(\sigma_1+\sigma_2)$, and $\bar{l}_1\equiv 0$ by definition. Note that the effect of gravity on the variable l_2 is included in the interface potential $V(l)$ to the extent that $L=L_A$ may be treated as a constant. Additional terms due to gravity arise from the fluctuations of L. If one wants to include those terms in a consistent manner, one has to treat all three interfaces in Fig. 2(a) simultaneously.

It is not difficult to find a linear transformation from l_1,l_2 to new variables h_1,h_2 such that the free energy (6.25) becomes diagonal, i.e.,

$$\begin{aligned}F\{l_1,l_2\}=\int d^2x[\,&\tfrac{1}{2}(\nabla h_1)^2+\tfrac{1}{2}\omega_1h_1^2\\&+\tfrac{1}{2}(\nabla h_2)^2+\tfrac{1}{2}\omega_2h_2^2]\,.\end{aligned} \tag{6.26}$$

The correlation function $C_1(q)$ defined by (6.24) can now be expressed in terms of the correlations of h_1 and h_2. This yields

$$C_1(q)=\frac{k_BTa_{11}^2}{q^2+\omega_1}+\frac{k_BTa_{12}^2}{q^2+\omega_2}\,, \tag{6.27}$$

i.e., the sum of two Lorentzians. The coefficients a_{11} and a_{12} in (6.27) depend on σ_1, σ_2, $\xi_\parallel$, and κ_1. For the experiments, discussed here, the correlation length $\xi_\parallel$ will usually be much smaller than the capillary length κ_1. In this case, one finds

$$a_{11}^2 = 1/(\sigma_1+\sigma_2)\,,\qquad a_{12}^2 = \sigma_2/[\sigma_1(\sigma_1+\sigma_2)]\,, \tag{6.28}$$

and

$$\omega_1 = \xi_\parallel^{-2}\,,\qquad \omega_2 = \sigma_1\kappa_1^{-2}/(\sigma_1+\sigma_2)\,, \tag{6.29}$$

to leading order in $\xi_\parallel/\kappa_1$. Since $\omega_1 = \xi_\parallel^{-2} \gg \omega_2$, the width of $C_1(q)$ as given by (6.28) is mainly determined by $\xi_\parallel^{-2}$. Thus, this length scale should also show up in the diffuse intensity (6.23) from a fluctuating liquid-vapor interface on top of a gravity-thinned layer as shown in Figs. 2(a) and 2(b).

C. Dispersion relation for capillary waves

In the preceding sections, the capillary waves have been treated as "static" interfacial configurations. In this final section, their dynamical properties will be briefly studied in the framework of classical hydrodynamics. Let us first consider the gravity-thinned layer shown in Fig. 2(c). Both liquid phases A and B are taken to be incompressible and their viscosities are neglected. Their motion is then governed by the Navier-Stokes equations

$$\bar{\rho}_\alpha \frac{d}{dt}\mathbf{v} = -\nabla p + \rho_\alpha \nabla U\,, \tag{6.30}$$

where $\alpha = A,B$. $\mathbf{v}$ and p are the velocity and the pressure. As before, $\bar{\rho}$ and ρ denote the mass and the number densities. ∇U is the force which acts on one fluid particle due to the interactions with the solid and with the rest of the fluid. At the solid surface [see Fig. 2(c)], one has the boundary condition that the normal component of $\mathbf{v}$ is zero.

As usual,[83] it is assumed that the deviations $\delta(\mathbf{x}) = l(\mathbf{x}) - \bar{l}$ of the interface from its equilibrium position are small. This assumption is justified for the three-dimensional systems considered here since the interfacial roughness $\xi_\perp$ is small compared to $\bar{l}$; see (6.18). For $\delta = 0$, the potential U which acts on the fluid molecules depends only on the distance z from the solid surface since the unperturbed system is translationally invariant parallel to it. Thus, one has $U(\mathbf{x}) = U(z) + O(\delta)$. Following standard arguments,[83] one then finds the dispersion relation

$$\omega^2(q) = q\left[\sigma_{AB}q^2 + (\rho_A-\rho_B)\left.\frac{\partial U(z)}{\partial z}\right|_{z=\bar{l}}\right] \times \frac{\tanh(q\bar{l})}{\bar{\rho}_A + \bar{\rho}_B\tanh(q\bar{l})} \tag{6.31}$$

for capillary waves with wave number q.

$\partial U(z)/\partial z\,|_{z=\bar{l}}$ may be expressed in terms of the interface potential $V(l)$. Consider the work per unit area required to shift the interface from its equilibrium position $l = \bar{l}$ to $l = \bar{l} + \delta$. This work is

$$\int_{\bar{l}}^{\bar{l}+\delta} dz(\rho_A-\rho_B)[U(z)+O(\delta)]\,.$$

On the other hand, this work is also given by the free-energy difference $V(\bar{l}+\delta) - V(\bar{l})$. As a consequence, one finds

$$(\rho_A-\rho_B)\left.\frac{\partial U(z)}{\partial z}\right|_{z=\bar{l}} = \left.\frac{\partial^2 V(l)}{\partial l^2}\right|_{l=\bar{l}} = \sigma_{AB}\xi_\parallel^{-2}\,, \tag{6.32}$$

where (3.4c) has been used in the last equality. If (6.32) is inserted in (6.31), one obtains the dispersion relation

$$\omega^2(q) = \sigma_{AB}q(q^2+\xi_\parallel^{-2})\frac{\tanh(q\bar{l})}{\bar{\rho}_A + \bar{\rho}_B\tanh(q\bar{l})} \tag{6.33}$$

for capillary waves on the A-B interface which bounds the gravity-thinned wetting layer [see Fig. 2(c)].

Exactly the same arguments may be used to derive the corresponding relations for capillary waves on the liquid-vapor interface of adsorbed liquid layers (see Fig. 1). In this case, the vapor density $\bar{\rho}_V \simeq 0$ may be neglected, which yields

$$\omega^2(q) = (\sigma_{LV}/\bar{\rho}_L)q(q^2+\xi_\parallel^{-2})\tanh(q\bar{l})\,. \tag{6.34}$$

The dispersion relations (6.33) and (6.34) could be studied by techniques similar to those which have already been used for free fluid-fluid interfaces.[84] In summary, the correlation length $\xi_\parallel$ should be observable both in the small-angle scattering of light and in experiments which measure the dispersion relations (6.33) or (6.34).

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