

Order of wetting transitions

S. Dietrich

Sektion Physik der Universität München, Theresienstrasse 37, D-8000 München 2, Federal Republic of Germany

M. Schick

Department of Physics (FM-15), University of Washington, Seattle, Washington 98195

(Received 3 October 1985)

We present general analytic expressions which permit the determination of the order of wetting transitions in mean-field theory for three systems of current interest: a one-component fluid near a wall, a binary liquid mixture near a wall, and a binary liquid mixture at three-phase coexistence. The underlying atomic forces are taken to be of the realistic long-range van der Waals type. These analytic results are derived by employing the sharp-kink approximation which replaces smooth density profiles by piecewise constant ones. In all those cases in which our analytic predictions can be compared with the numerical results for the full inhomogeneous mean-field equations there is agreement between them.

I. INTRODUCTION

Recent theoretical work on the wetting transition, both in adsorbed systems and in binary liquid mixtures, has focused on determining the conditions under which this transition is first-order or continuous.¹⁻¹⁷ For physically relevant systems, the treatment of this problem requires *all* interactions in the problem to be of the long-range van der Waals type.^{14,15} This is assumed throughout this paper. For a one-component fluid^{8,11,15,18} and binary liquid mixtures¹⁹ with such forces, it has been shown that the wetting transitions are *not* driven by interface fluctuations. There is strong evidence that in the case of a continuous wetting transition ("critical wetting") mean-field theory (MFT) predicts correctly the critical exponents associated with such a transition.^{15,18,19} The most obvious question, however, is how the order of the transition varies as a function of the atomic forces. The general determination of the separatrix between first- and second-order wetting is a subtle problem even in MFT due to the inhomogeneity of the system and the long-range character of the forces.

The purpose of this paper is to present an analytic answer to this question within MFT. However, one should keep in mind that even though, as mentioned above, the fluctuations do not affect the critical exponents, one has to expect that they do affect the separatrix between first- and second-order transitions. This can be important for a comparison with experimental results. To date, there have been no reliable calculations which incorporate properly the effect of fluctuations on the order of the wetting transitions in systems with long-range forces. Monte Carlo calculations²⁰⁻³⁰ and molecular dynamics^{31,32} have already been applied to the wetting problem. But they were not used to investigate the order of the transition for the realistic long-range forces in three-dimensional space. Our results can serve as a starting point for such calculations, and it would be interesting

to determine how sensitive to fluctuations the separatrix actually is.

Most calculations have been performed for the one-component fluid near a wall (Refs. 1-3, 5, 6, and 8-17). As reviewed more fully in Sec. II below, it can be concluded that both first- and second-order transitions can occur.¹⁴⁻¹⁶ What actually results depends crucially on the next-to-leading-order terms in an expansion of the surface thermodynamic potential for large coverage.

It is easier to observe experimentally interfacial wetting transitions in binary liquid mixtures and several elegant experiments have been performed. (They will be discussed in the summary.) However, only Tarazona *et al.*⁴ addressed the question of the order of the transition in these more complex systems with all forces being long ranged. Because the Hamiltonian parameter space is so large, Tarazona *et al.* confined their calculations to a small subspace in which they were able to locate numerically the separatrix between first-order and critical wetting as determined by their mean-field equations. In this paper, we determine this separatrix analytically within the full parameter space. This enables us to display explicitly the crucial role of the next-to-leading-order potential terms in determining the order of the transition. The similarity of our treatment of the one-component fluid-wall case (Sec. II) and of the binary liquid mixtures (Sec. III) emphasizes the similarity of these systems. In particular, the surface free energy $\Omega_s(l)$ of each has the same expansion in terms of a one-component order parameter l^{-1} , the inverse of the thickness of the wetting layer, for large l . The differences between the two systems reside in the coefficients of this expansion which depend on far more parameters in the binary liquid mixture than in the one-component fluid-wall case.

In wetting experiments with binary liquid mixtures one can observe not only the wetting of the gas-liquid interface but also the wetting of a wall by the binary liquid mixture. With such an experiment, for example, a

prewetting line has been found.³³ There are only a few calculations about this type of wetting.^{34,35} We discuss it in Sec. IV.

Our analytic results follow from the use of the sharp-kink approximation. We find that in the limited subspace considered by Tarazona *et al.* this approximation predicts the location of the separatrix to within the accuracy of the numerical solution. Such an agreement is also found for two calculations for the one-component fluid near a wall. Indeed there is reason to believe that if one is not too close to T_c this approximation gives the same separatrix as the numerical solution of the full mean-field equations (MFE's).¹⁶

II. ONE-COMPONENT FLUID NEAR A WALL

We consider the grand canonical potential $\Omega[\{\rho(\mathbf{r})\}, T, \mu]$ which is a functional of the number density $\rho(\mathbf{r})$ and a function of the temperature T and of the chemical potential μ . Within MFT it is given by

$$\begin{aligned} \Omega[\{\rho(\mathbf{r})\}, T, \mu] = & \int d^3r f_h[\{\rho(\mathbf{r})\}, T] \\ & + \frac{1}{2} \int d^3r \int d^3r' \tilde{w}(|\mathbf{r}-\mathbf{r}'|) \rho(\mathbf{r}) \rho(\mathbf{r}') \\ & + \int d^3r [\rho_w V(\mathbf{r}) - \mu] \rho(\mathbf{r}). \end{aligned} \quad (2.1)$$

All integrals are taken over the half-space $V_+ = \{\mathbf{r} = (\mathbf{r}_\parallel, z \geq 0)\}$.

The first term is the free-energy functional of a fluid system which contains only short-range, hard-core interactions. It is evaluated here in a local density approximation so that any spatial oscillations of the density, as to be expected close to a hard wall, are ignored. These oscillations affect the surface free energy most strongly for low coverage. Therefore, they are important to locate the transition temperature T_w for a first-order transition^{36,37} because in this case T_w depends not only on the asymptotic behavior of the surface free energy for large coverage but on all its details. For just that reason, however, we expect that they have only a mild influence on the separatrix and on T_w of critical wetting. It would be interesting to check this, but we do not pursue this point further; for interfacial wetting in binary fluid mixtures these effects are probably absent.

The long-range part of the fluid-fluid interaction is given by $\tilde{w}(|\mathbf{r}-\mathbf{r}'|)$ while the fluid-wall potential is $\rho_w V(\mathbf{r})$, with ρ_w the mean number density of the wall. In the following we take $V(\mathbf{r}) = V(z)$ neglecting corrugation effects. They vanish exponentially fast,³⁸ and therefore they should be important only for details of a first-order transition. Within this approximation all one-point correlation functions depend only on z . The wall is in the x - y plane at $z=0$.

Minimization of $\Omega[\{\rho(\mathbf{r})\}, T, \mu]$ with respect to the density profile $\rho(\mathbf{r})$ yields the mean-field value of the grand canonical potential $\Omega(T, \mu)$ and the equilibrium profile $\rho(\mathbf{r}, T, \mu) = \rho(z, T, \mu)$. In the sharp-kink approximation, we seek the minimum of Eq. (2.1) in the restricted subspace of piecewise constant $\rho(z)$. In particular we choose [see Fig. 1(a)]

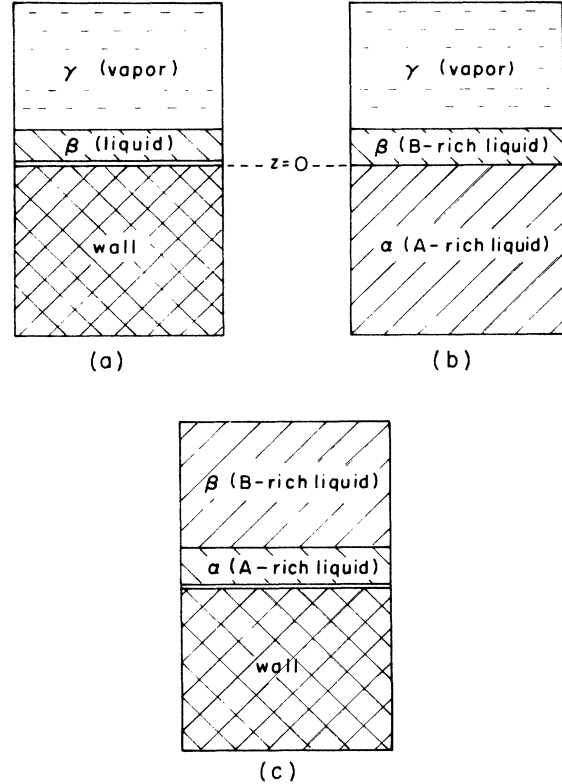


FIG. 1. Wetting phenomena considered in Secs. II, III, and IV. (a) One-component system (β, γ) close to a wall. The gap between the liquid phase (β) and the wall indicates the excluded volume $d_w > 0$. β and γ are assumed to be at coexistence. (b) Binary liquid mixture (α, β, γ) at the triple line. The intruding liquid film is assumed to be B rich. The A -rich liquid plays the role of the wall in (a). (c) Binary liquid mixture (α, β) close to a wall. To be concrete it is assumed that the α (β) phase is the A - (B -) rich liquid. The two liquids are at coexistence and off the triple line. Various other combinations are possible.

$$\rho(z) = \begin{cases} \rho_\beta, & d_w \leq z \leq l \\ \rho_\gamma, & l < z \leq L \\ 0, & \text{otherwise.} \end{cases} \quad (2.2)$$

Thus, l is the apparent thickness of the layer of liquid of density ρ_β between the wall and the gas of density ρ_γ . Due to the hard-core part of the interaction between fluid and wall, the density of the liquid film vanishes at distances smaller than a microscopic distance d_w .¹⁴ For convenience, we have cut off the gas phase at a macroscopic distance L .

Upon substitution of the sharp-kink profile, Eq. (2.2), into Eq. (2.1), one finds that the grand canonical potential functional separates into the following bulk and surface contributions (A denotes the surface area):

$$\Omega[\{\rho(\mathbf{r})\}, T, \mu] = AL\Omega_b(\rho_\gamma, T, \mu) + A\Omega_s(l, T, \mu), \quad (2.3)$$

where

$$\Omega_b(\rho_\gamma, T, \mu) = f_h(\rho_\gamma, T) + \frac{1}{2}\rho_\gamma^2 \int_{-\infty}^{\infty} dx w(|x|) - \mu\rho_\gamma, \quad (2.4)$$

and

$$w(x) = \int d^2 r_{||} \tilde{w}[(r_{||}^2 + x^2)^{1/2}] \quad (2.5)$$

The actual density ρ_γ is obtained by minimizing the bulk contribution with respect to ρ_γ . It yields the gas density as obtained within MFT. The liquid density ρ_β is obtained similarly. With these densities determined, the only profile parameter upon which the surface contribution Ω_s depends and which can be varied is the thickness l . The surface contribution can be written (we suppress the arguments T and μ)

$$\Omega_s(l) = \sigma_{\gamma, \text{vac}} + l[\Omega_b(\rho_\beta) - \Omega_b(\rho_\gamma)] + \sigma_{\beta, \gamma} + \sigma_{w, \beta} + \omega(l), \quad (2.6)$$

where vac stands for vacuum. The first term is simply the surface tension $\sigma_{\gamma, \text{vac}}$, which is caused by truncating the bulk gas phase at the surface of convenience $z=L$. This is

$$\sigma_{\gamma, \text{vac}} = -\frac{1}{2}\rho_\gamma^2 \int_0^\infty dy t(y), \quad (2.7)$$

where

$$t(y) := \int_y^\infty dx w(x). \quad (2.8)$$

The second term, the difference in grand canonical potentials per unit volume of the liquid and gas phases multiplied by the nominal length of the film, is just the bulk free energy needed to replace a slab of gas by an equal volume of (metastable) liquid. This contribution vanishes at coexistence where the grand canonical potentials of the gas and the liquid are equal. The additional contributions do not vanish at coexistence and are the free energies associated with creating the liquid-gas interface and the wall-liquid interface. If l were infinite so that these two interfaces did not interact with another, these free energies would be

$$\sigma_{\beta, \gamma} = -\frac{1}{2}(\rho_\beta - \rho_\gamma)^2 \int_0^\infty dy t(y), \quad (2.9)$$

and

$$\sigma_{w, \beta} = -\frac{1}{2}\rho_\beta^2 \int_0^\infty dy t(y) - \Omega_b(\rho_\beta)d_w + \rho_\beta \rho_w \int_{d_w}^\infty dy V(y). \quad (2.10)$$

$\sigma_{\beta, \gamma}$ is the sharp-kink approximation for the familiar gas-liquid surface tension. In MFT $\rho_\beta - \rho_\gamma \sim \tau^{1/2} \rightarrow 0$, with $\tau \equiv (T_c - T)/T_c$, so that in the sharp-kink result of Eq. (2.9), $\sigma_{\beta, \gamma} \sim \tau$. However, if this approximation is not employed and the liquid-gas interface is allowed to vary smoothly over distances of the order of the (large) bulk correlation length, then MFT yields $\sigma_{\beta, \gamma} \sim \tau^{3/2}$. Obviously the difference stems from the fact that in the sharp-kink approximation the correlation length $\xi \sim \tau^{-1/2}$ has been put to zero. So, at first glance, it makes sense only to apply the sharp-kink approximation in those cases where T_w is not too close to T_c . However, this argument only shows that the asymptotic value of $\Omega_s(l)$ for infinite l is given poorly by the sharp-kink approximation for T near T_c . We are concerned with the order of the wetting transition which depends upon the approach of $\omega(l)$ to its asymptotic value which is zero. Concerning this point,

nothing is known rigorously. However, from the work of Ref. 15 we know that the order of the transition and the transition temperature of the critical wetting as given by the sharp-kink approximation and the full solution of the inhomogeneous MFE's are the same for a particular case of $(T_c - T_w)/T_c = 0.2$. A similar agreement is found in the appendix for a critical wetting in a binary liquid mixture at a temperature $(T_{\text{cep}} - T_w)/T_{\text{cep}} < 0.1$ where T_{cep} is the critical end point temperature. These results indicate that the sharp-kink approximation for $\omega(l) = \Omega(l) - \Omega(\infty)$ is far better than for $\Omega(\infty)$ and hence $\Omega(l)$ itself. The last term in Eq. (2.6) is the correction to the surface free energy which is necessary if l is not infinite:

$$\omega(l) = (\rho_\beta - \rho_\gamma) \left[\rho_\beta \int_{l-d_w}^\infty dy t(y) - \rho_w \int_l^\infty dy V(y) \right]. \quad (2.11)$$

At coexistence, $\omega(l)$ carries the only dependence of the grand canonical potential on the film thickness and thus determines whether the wall-gas interface is wetted by the liquid or is not. The former occurs at some temperature T_w if $\omega(l)$ has a global minimum at infinite l ; the latter occurs otherwise.

We now take all interactions in the problem to be of the long-range van der Waals type so that, for large distances and ignoring retardation,

$$V(z) = -(u_3/z^3 + u_4/z^4 + \dots) \text{ for } z \gg d_w, \quad (2.12)$$

which defines the coefficients u_3, u_4 , and

$$t(z) = -(t_3/z^3 + t_4/z^4 + \dots) \text{ for } z \gg d_w, \quad (2.13)$$

which defines t_3, t_4 . With these definitions, $\omega(l)$ takes the form¹⁵ for large l

$$\omega(l) = a/l^2 + b/l^3 + \dots, \quad (2.14)$$

with¹³

$$a = \frac{1}{2}(\rho_\beta - \rho_\gamma)(u_3\rho_w - t_3\rho_\beta), \quad (2.15)$$

and

$$b = \frac{1}{3}(\rho_\beta - \rho_\gamma)[u_4\rho_w - (t_4 + 3d_w t_3)\rho_\beta]. \quad (2.16)$$

In order that critical wetting occurs at $T = T_w$, the coefficient $a(T)$ must be negative for $T < T_w$ and must vanish at that temperature. As ρ_β is always greater than ρ_γ ,³⁹ and ρ_β can only vary between its value at the triple point $\rho_\beta(T_t)$ and the critical density $\rho_c = \rho_\beta(T_c)$, the coefficient $a(T)$ can only fulfill the above mentioned conditions provided that

$$\rho_c/\rho_w < u_3/t_3 < \rho_\beta(T_t)/\rho_w. \quad (2.17)$$

This is a necessary, but not sufficient, condition for critical wetting to occur. The order of the transition is determined by the higher-order coefficients in the expansion of $\omega(l)$. The transition will be first-order if b is negative at T_w and can be continuous if b is positive.⁴⁰ At T_w , $a(T_w) = 0$ so that

$$\rho_\beta(T_w)/\rho_w = u_3/t_3 \quad (2.18)$$

and

$$b(T_W) = \frac{1}{3}(\rho_\beta - \rho_\gamma)\rho_w u_3(u_4/u_3 - t_4/t_3 - 3d_w). \quad (2.19)$$

Thus we find within the sharp-kink approximation that the wetting transition can be second-order if

$$t_4/t_3 + 3d_w < u_4/u_3, \quad (2.20)$$

and is first-order if the inequality is reversed. The separatrix between first- and second-order wetting transitions, the locus of tricritical wetting transitions,^{2,16} is given by

$$u_4/u_3 = t_4/t_3 + 3d_w. \quad (2.21)$$

Kroll and Meister¹⁴ solved numerically the MFE which results from minimizing the grand canonical potential of Eq. (2.1) in the full subspace of functions in which $\rho(\tau) = \rho(z)$. They chose pure Lennard-Jones potentials for which $u_3, t_3 > 0$ and $u_4 = t_4 = 0$. In accordance with Tarazona and Evans³ they found first-order transitions only. This result of the numerical solution of the full MFE is in agreement with the simple prediction of the sharp-kink approximation, Eq. (2.21), because $d_w > 0$. This approximation works equally well in the case in which the long-range parts of all potentials are treated in the Kac limit.⁴ [One has, e.g., $V_{lr}(z) = \hat{V}_{lr}(\gamma z)$ with the limit $\gamma \rightarrow 0$ to be taken; $V(z) = V_{sr}(z) + V_{lr}(z)$, with $V_{sr}(z) = 0$ for $z \geq d_w$ and $V_{sr}(z) = \infty$ for $z < d_w$. A similar partition holds for $t(z)$ with d_w replaced by d .] The solution of the MFE in that limit corresponds to the solution of the MFE without that limit but with the original potentials shifted by the amount of the hard-core radius of the substrate potential d_w and of the fluid-fluid interaction d , respectively. So the MFT for the Kac limit of potentials V and t amounts to the MFT for new potentials \tilde{V}, \tilde{t} without the Kac limit. The sharp-kink approximation can then be applied to the latter potentials. As a result of the Kac limit the density no longer vanishes for $z < d_w$ but for $z < 0$. For pure Lennard-Jones potentials V and t one has

$$\begin{aligned} \tilde{V}(z) &= -u_3(z + d_w)^{-3} + O(z^{-5}) \\ &= -\tilde{u}_3 z^{-3} - \tilde{u}_4 z^{-4} + O(z^{-5}), \end{aligned} \quad (2.22)$$

with $\tilde{u}_3 = u_3$, $\tilde{u}_4 = -3d_w u_3$ and

$$\begin{aligned} \tilde{t}(z) &= -t_3(z + d)^{-3} + O(z^{-5}) \\ &= -\tilde{t}_3 z^{-3} - \tilde{t}_4 z^{-4} + O(z^{-5}), \end{aligned} \quad (2.23)$$

with $\tilde{t}_3 = t_3$, $\tilde{t}_4 = -3dt_4$. According to Eq. (2.21) the separatrix between first- and second-order transitions is therefore given by

$$d_w = d. \quad (2.24)$$

If one studies pure Lennard-Jones potentials in the Kac limit, the wetting transition should, according to the criterion given above, be first-order for $d/d_w < 1$ and second-order for $d/d_w > 1$. Kroll and Meister¹⁴ solved this problem numerically and found the first-order transitions for $\lambda = \sigma/\sigma_s < 1$ and the second-order transitions for $\lambda > 1$, where σ and σ_s are the Lennard-Jones parameters of their fluid-fluid and fluid-wall pair potentials, respectively. This is in agreement with our prediction if $d = \sigma$ and if $d_w = \frac{1}{2}(\sigma + \sigma_s)$ which is the choice of Kroll and Meister. We regard this as a satisfactory check of the

separatrix line $\lambda = 1$ as predicted by the sharp-kink approximation. Not only does this approximation predict the order of the transition but it also predicts the value of the T_W for critical wetting via Eq. (2.18). [See the appendix and Ref. 15. The prediction of T_W for a first-order transition based on the sharp-kink approximation is less accurate because in that case the details of the higher-order terms in Eq. (2.14) do matter, and they are sensitive to the difference between a smooth and a sharp kink.] Unfortunately, with respect to that, the published data of Kroll and Meister¹⁴ are not sufficient to compare them with our analytic results.

At first glance the condition for critical wetting as given by Eq. (2.20) seems to differ by the term $3d_w$ from the condition as given by Eq. (6) in Ref. 15. But the following arguments show that for the same substrate potential V and the same fluid-fluid pair potential \tilde{w} the lattice theory in Ref. 15 and the continuum theory as presented here give the identical separatrix. The *only* difference between the approach in Ref. 15 and the present one is that in Ref. 15 the fluid atoms are restricted to sit on lattice sites with a lattice parameter a . With $z = na$, $n = 1, 2, \dots$, Eq. (2.12) gives

$$V_{\text{latt}}(n) = -(u_3^{\text{latt}} n^{-3} + u_4^{\text{latt}} n^{-4} + \dots), \quad (2.25)$$

where $u_3^{\text{latt}} = u_3 a^{-3}$ and $u_4^{\text{latt}} = u_4 a^{-4}$. On the other hand,

$$\begin{aligned} t_{\text{latt}}(n) &= \sum_{m=0}^{\infty} w_{\text{latt}}(n+m) \\ &= -(t_3^{\text{latt}} n^{-3} + t_4^{\text{latt}} n^{-4} + \dots), \end{aligned} \quad (2.26)$$

with

$$w_{\text{latt}}(k) = \sum_{n=-\infty}^{\infty} \sum_{m=-\infty}^{\infty} \tilde{w}[a(n^2 + m^2 + k^2)^{1/2}]. \quad (2.27)$$

Using the Euler-MacLaurin summation formula one gets for

$$\tilde{w}(r) = -(Ar^{-6} + Br^{-7} + \dots)$$

the results

$$t_3^{\text{latt}} = t_3 a^{-6} \quad (2.28)$$

and

$$t_4^{\text{latt}} = (t_4 + \frac{3}{2}at_3)a^{-7}. \quad (2.29)$$

The extra term $\frac{3}{2}at_3$ stems from the discrete lattice in the half-space $z > 0$. In the lattice version, the condition for critical wetting is¹⁵

$$t_4^{\text{latt}}/t_3^{\text{latt}} < u_4^{\text{latt}}/u_3^{\text{latt}}. \quad (2.30)$$

Using Eqs. (2.28) and (2.29) one finally arrives at

$$t_4/t_3 + 3a/2 < u_4/u_3. \quad (2.31)$$

In the lattice description the sharp-kink approximation is set up in such a way that the density is zero in the lattice planes $n = 0, -1, -2, \dots$, that it is liquidlike in the lattice planes $n = 1, 2, \dots, l$, and it is gaslike for

$n = l + 1, l + 2, \dots$. This corresponds to the interface positions at $z = a/2$ and $z = (l + \frac{1}{2})a$.⁴¹ Therefore, we can conclude

$$d_w = a/2. \quad (2.32)$$

Equation (2.31) together with Eq. (2.32) is identical to Eq. (2.20) and shows that the lattice theory and the continuum theory give the same separatrix. Equation (2.32), of course, holds only as long as the mean distance between the fluid atoms is about the same as between a fluid atom and the wall. If one would like to drop this restriction in the lattice model, one would have to introduce repulsive forces to accommodate two microscopic length scales on the lattice. However, as Eq. (2.32) shows, this is not necessary to incorporate the excluded volume $d_w > 0$.⁴² That means that in Ref. 15 the existence of critical wetting was shown even in the presence of an excluded volume.

It is worth noting here that what can be concluded from the above is that the wetting transition of a fluid near a wall would be first-order if the substrate potential were of the 3–9 and the fluid-fluid pair potential of the 6–12 Lennard-Jones form [see Eqs. (2.12), (2.13), and (2.20)]. However, as emphasized in Ref. 15, this is not the case in real systems. In particular, the coefficients u_4 and t_4 are affected by many-body forces, by adsorption of a monolayer of impurity atoms at the surface,¹⁶ and by formation of a few layers of solid at the surface. The latter is to be expected for strong substrates. The coefficient u_4 certainly depends also on the structure of the substrate orthogonal to the surface. For the sake of argument, let us make the crude assumption that $V(z)$ can be written as a sum of 6–12 Lennard-Jones potentials \tilde{w}_s between a fluid atom and a substrate atom located at a lattice site in the half-space $z < 0$. With $\tilde{w}_s(r) = -Ar^{-6} + O(r^{-8})$ one gets

$$V(z) = -(\pi/4)Aa_{\parallel}^{-2}a_{\perp}^{-4} \sum_{n=0}^{\infty} (n + z/a_{\perp})^{-4} + O(z^{-5}). \quad (2.33)$$

$a_{\perp}(a_{\parallel})$ is the lattice constant of the substrate orthogonal (parallel) to the surface. From Eq. (2.33) one can derive that $u_4/u_3 = 3a_{\perp}/2$. If the fluid-fluid interaction would be purely of the Lennard-Jones form, then $t_4 = 0$. Then the condition for critical wetting [Eq. (2.20)] is $d_w < a_{\perp}/2$. In the simplest model d_w is the sum of the atomic radii of the substrate atom and of the fluid atom and $a_{\perp}/2$ equals the atomic radius of the substrate atom so that this inequality is not fulfilled.⁴³ However, this estimate is crude.

It does show that to the physical factors discussed above which can influence the order of the wetting transition must be added the structure of the substrate orthogonal to the surface. We reiterate that there is no reason to expect *a priori* that the wetting transition need be first-order.

It is tempting to extend the application of Eqs. (2.6)–(2.16) from the gas-liquid coexistence curve of the adsorbate to the sublimation or melting curve of the adsorbate so that the substrate now is wetted by a solid. The first problem one encounters in these cases are strain effects caused by a mismatch between the lattice constants of the substrate and the adsorbate and/or the compression of the adsorbate due to the substrate potential. This adds a linear term to $\omega(l)$ in Eq. (2.14) which prevents it from having a global minimum for infinitely thick films.^{44,45} But even if these effects are small, one is left with the fundamental problem of which variational functional Ω describes properly the sublimation and melting transition in the bulk of the adsorbate. If that were known, then one would introduce in addition a substrate potential $V(z)$ and study the corresponding wetting transitions. $\omega(l)$ would then be given by a sharp-kink approximation for such a theory. Ebner⁴⁶ and Pandit and Fisher⁴⁷ discussed the possible influence of a triple point on wetting phase diagrams, but we are not aware of any serious quantitative study of these kinds of wetting transitions. Therefore, within the framework of the functional Ω as given by Eq. (2.1) there is no triple point, and in Eq. (2.17) $\rho_{\beta}(T_i)$ has to be interpreted as $\rho_{\beta}(0)$, the MFT value of ρ_{β} at zero temperature.

III. BINARY LIQUID MIXTURES

Consider a fluid which is a mixture of A atoms and B atoms. The aim of this section is to express the grand canonical potential of such a binary fluid mixture in terms of the thickness l of a film of B -rich liquid at the interface between vapor and A -rich liquid. In particular, we will again obtain, within the sharp-kink approximation, an expression of the form

$$\Omega(l) = \Omega(\infty) + al^{-2} + bl^{-3} + \dots, \quad (3.1)$$

just as in the case of a one-component fluid near a wall, with explicit expressions for the coefficients a and b which are the analogues of Eqs. (2.15) and (2.16). The binary liquid mixture is complicated by the fact that each phase is characterized by two densities instead of one.

We begin with the grand canonical potential functional ($i = 1, 2$)

$$\Omega[\{\rho_i(\mathbf{r}), T, \mu_i\}] = \int d^3r f_h[\{\rho_i(\mathbf{r}), T\}] + \frac{1}{2} \sum_{i,j} \int d^3r \int d^3r' \tilde{w}_{ij}(|\mathbf{r} - \mathbf{r}'|) \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') - \sum_i \mu_i \int d^3r \rho_i(\mathbf{r}), \quad (3.2)$$

where $\rho_i(\mathbf{r})$ is the particle density of the i th species and the other symbols are as before. We minimize this expression in the subspace of piecewise constant $\rho_i(\mathbf{r})$. We choose

$$\rho_i(\mathbf{r}) = \begin{cases} \rho_{i,\alpha}, & -L/2 \leq z < 0 \\ \rho_{i,\beta}, & 0 \leq z \leq l \\ \rho_{i,\gamma}, & l < z \leq L/2. \end{cases} \quad (3.3)$$

The α phase can be thought of as the A -rich liquid, the β phase as the B -rich liquid, and γ as the vapor; see Fig. 1(b). The cutoffs at $z = \pm L/2$ are only for convenience. If the hard-core radii of all interactions were the same, the above would be just a continuum version of the Blume-Emery-Griffiths model.^{48,49} We do not use this restriction because the order of the transition turns out to depend on these details. But to emphasize the similarity with this model, we take as independent variables

$$M(\mathbf{r}) := \rho_1(\mathbf{r}) - \rho_2(\mathbf{r}) \quad (3.4a)$$

and

$$Q(\mathbf{r}) := \rho_1(\mathbf{r}) + \rho_2(\mathbf{r}). \quad (3.4b)$$

M denotes the stoichiometric composition and Q the overall number density. The ansatz of Eq. (3.3) then becomes

$$M(\mathbf{r}) = \begin{cases} M_\alpha, & -L/2 \leq z < 0 \\ M_\beta, & 0 \leq z \leq l \\ M_\gamma, & l < z \leq L/2, \end{cases} \quad (3.5)$$

with a similar expression for $Q(\mathbf{r})$. We also define the analogous fields

$$H := \frac{1}{2}(\mu_1 - \mu_2) \quad (3.6a)$$

and

$$\Delta := -\frac{1}{2}(\mu_1 + \mu_2), \quad (3.6b)$$

and couplings

$$\tilde{J}(\mathbf{r}) := -\frac{1}{4}[\tilde{w}_{11}(\mathbf{r}) - 2\tilde{w}_{12}(\mathbf{r}) + \tilde{w}_{22}(\mathbf{r})], \quad (3.7a)$$

$$\tilde{K}(\mathbf{r}) := -\frac{1}{4}[\tilde{w}_{11}(\mathbf{r}) + 2\tilde{w}_{12}(\mathbf{r}) + \tilde{w}_{22}(\mathbf{r})], \quad (3.7b)$$

$$\tilde{C}(\mathbf{r}) := -\frac{1}{4}[\tilde{w}_{11}(\mathbf{r}) - \tilde{w}_{22}(\mathbf{r})]. \quad (3.7c)$$

Then, within the sharp-kink approximation of Eq. (3.2), the grand canonical potential can be separated into bulk and surface contributions

$$\Omega[\{\rho_i(\mathbf{r})\}] = AL\frac{1}{2}[\Omega_b(M_\alpha, Q_\alpha) + \Omega_b(M_\gamma, Q_\gamma)] + A\Omega_s, \quad (3.8)$$

where A is the surface area of the flat interface and

$$\Omega_b(M, Q) = f_h(M, Q) - \frac{1}{2}(M^2\hat{J} + Q^2\hat{K} + 2QM\hat{C}) - HM + \Delta Q, \quad (3.9a)$$

with

$$\hat{J} = \int d^3r \tilde{J}(\mathbf{r}), \quad (3.9b)$$

and similarly for \hat{K} and \hat{C} .

The bulk densities M and Q are obtained as usual by minimizing Ω_b with respect to them. The surface contribution to Eq. (3.8), Ω_s , can be put in the form

$$\Omega_s = \sigma_{\alpha, \text{vac}} + \sigma_{\gamma, \text{vac}} + l[\Omega_b(M_\beta, Q_\beta) - \Omega_b(M_\gamma, Q_\gamma)] + \sigma_{\alpha, \beta} + \sigma_{\beta, \gamma} + \omega(l). \quad (3.10)$$

The first two terms are, again, simply the energy needed

to truncate the bulk phases α and γ at the surfaces of convenience at $z = \pm L/2$.

$$\sigma_{\alpha, \text{vac}} = \frac{1}{2}M_\alpha^2 J(0) + \frac{1}{2}Q_\alpha^2 K(0) + M_\alpha Q_\alpha C(0), \quad (3.11)$$

and similarly for $\sigma_{\gamma, \text{vac}}$, where

$$J(l) = -\frac{1}{4} \int_l^\infty dy [t_{11}(y) - 2t_{12}(y) + t_{22}(y)], \quad (3.12a)$$

$$K(l) = -\frac{1}{4} \int_l^\infty dy [t_{11}(y) + 2t_{12}(y) + t_{22}(y)], \quad (3.12b)$$

$$C(l) = -\frac{1}{4} \int_l^\infty dy [t_{11}(y) - t_{22}(y)], \quad (3.12c)$$

and

$$t_{ij}(y) = \int_y^\infty dx \int d^2r_{\parallel} \tilde{w}_{ij}[(r_{\parallel}^2 + x^2)^{1/2}]. \quad (3.13)$$

The third term in Eq. (3.10) is just the bulk energy needed to replace a slab of thickness l of phase γ by phase β . This contribution vanishes at β - γ coexistence. (It is assumed throughout this section that we are at α - γ coexistence.) The terms $\sigma_{\alpha, \beta}$ and $\sigma_{\beta, \gamma}$ are the surface tensions for the interfaces between the bulk phases α, β and β, γ , respectively:

$$\sigma_{\alpha, \beta} = \frac{1}{2}(M_\alpha - M_\beta)^2 J(0) + \frac{1}{2}(Q_\alpha - Q_\beta)^2 K(0) + (Q_\alpha - Q_\beta)(M_\alpha - M_\beta)C(0), \quad (3.14)$$

and similarly for $\sigma_{\beta, \gamma}$. The last term in Eq. (3.10) for the surface potential is the correction to the surface free energies due to the finite thickness of l . It is

$$\begin{aligned} \omega(l) = & (M_\alpha - M_\beta)(M_\beta - M_\gamma)J(l) \\ & + (Q_\alpha - Q_\beta)(Q_\beta - Q_\gamma)K(l) \\ & + [(Q_\alpha - Q_\beta)(M_\beta - M_\gamma) \\ & + (M_\alpha - M_\beta)(Q_\beta - Q_\gamma)]C(l). \end{aligned} \quad (3.15)$$

As before, we are interested in the behavior of $\omega(l)$ for large l . If we define the expansion of the interactions $t_{ij}(z)$ as

$$t_{ij}(z) = -(t_{3,ij}z^{-3} + t_{4,ij}z^{-4} + \dots), \quad (3.16)$$

then

$$\omega(l) = al^{-2} + bl^{-3} + \dots, \quad (3.17)$$

where

$$\begin{aligned} \begin{Bmatrix} a \\ b \end{Bmatrix} = & (M_\alpha - M_\beta)(M_\beta - M_\gamma) \begin{Bmatrix} a_J \\ b_J \end{Bmatrix} \\ & + (Q_\alpha - Q_\beta)(Q_\beta - Q_\gamma) \begin{Bmatrix} a_K \\ b_K \end{Bmatrix} \\ & + [(Q_\alpha - Q_\beta)(M_\beta - M_\gamma) \\ & + (M_\alpha - M_\beta)(Q_\beta - Q_\gamma)] \begin{Bmatrix} a_C \\ b_C \end{Bmatrix}, \end{aligned} \quad (3.18)$$

and

$$a_J = (t_{3,11} - 2t_{3,12} + t_{3,22})/8, \quad (3.19a)$$

$$a_K = (t_{3,11} + 2t_{3,12} + t_{3,22})/8, \quad (3.19b)$$

$$a_C = (t_{3,11} - t_{3,22})/8, \quad (3.19c)$$

and

$$b_J = (t_{4,11} - 2t_{4,12} + t_{4,22})/12, \quad (3.20a)$$

$$b_K = (t_{4,11} + 2t_{4,12} + t_{4,22})/12, \quad (3.20b)$$

$$b_C = (t_{4,11} - t_{4,22})/12, \quad (3.20c)$$

Equations (3.17)–(3.20) are the analogues of Eqs. (2.14)–(2.16) which we sought and from which follow similar statements concerning critical wetting. In particular, necessary conditions for critical wetting are that $a(T < T_W) < 0$, $a(T_W) = 0$, and $b(T_W) > 0$.

Let us examine the coefficient a of Eq. (3.18) more closely in order to determine the conditions which favor critical wetting. First, as stated above $a(T)$ must be negative at low temperatures so that the α - γ interface is not wet at these temperatures. (To be specific we focus on simple binary liquids, i.e., those that mix at high temperatures and do not mix at low temperatures.) We first take the α phase to be the A -rich liquid ($A \equiv 1$) and the β phase to be the B -rich liquid ($B \equiv 2$); see Fig. 1(b). Thus at low temperatures we have for the total densities $Q = \rho_1 + \rho_2$ and for the density differences $M = \rho_1 - \rho_2$

$$Q_\alpha \rightarrow \rho_0^{(A)}, \quad M_\alpha \rightarrow \rho_0^{(A)}, \quad (3.21a)$$

$$Q_\beta \rightarrow \rho_0^{(B)}, \quad M_\beta \rightarrow -\rho_0^{(B)}, \quad (3.21b)$$

$$Q_\gamma \rightarrow 0, \quad M_\gamma \rightarrow 0. \quad (3.21c)$$

$\rho_0^{(A)}$ ($\rho_0^{(B)}$) denotes the total density of the A - (B -) rich liquid phase at low temperatures. Within the description of Eq. (3.2), $\rho_0^{(A)}$ ($\rho_0^{(B)}$) can be identified with the total density of the pure A (B) liquid at low temperatures. Equations (3.21) together with Eqs. (3.18) and (3.19) give at low temperatures

$$a \rightarrow -\frac{1}{2}\rho_0^{(B)}(\rho_0^{(B)}t_{3,BB} - \rho_0^{(A)}t_{3,AB}). \quad (3.22)$$

It is instructive to compare the result in Eq. (3.22) with the low-temperature limit of the same coefficient, call it a' , for the one-component fluid near a wall, Eq. (2.15):

$$a' \rightarrow -\frac{1}{2}\rho\beta(\rho_0^{(B)}t_3 - \rho_w u_3). \quad (3.23)$$

The comparison between Eq. (3.23) and Eq. (3.22) shows that in the case of interfacial wetting in binary liquid mixtures the role of the wall is played by that liquid phase on top of which the other liquid phase intrudes as a layer between the lower liquid and the vapor. (If the β phase is the A -rich liquid and the α -phase the B -rich liquid all A and B symbols in Eq. (3.22) must be interchanged; therefore, the above statement remains true also in this case.) The condition $a(T=0) < 0$ is given by Eq. (3.22) as

$$t_{3,AB}/t_{3,BB} < \rho_0^{(B)}/\rho_0^{(A)}, \quad (3.24)$$

if the intruding layer is B rich. This is strictly analogous to the right-hand side of the inequality in Eq. (2.17) for the one-component fluid system near a wall. Equation (3.24) states that an adsorbate (β) is not expected to wet a liquid (α) at low temperatures if the interaction between them ($t_{3,AB}$) is weaker than the adsorbate-adsorbate interaction ($t_{3,BB}$) [see Figs. 1(a) and 1(b)].

For critical wetting to occur, it is necessary, but not sufficient, that the coefficient $a(T)$ (i) is negative at low temperatures and (ii) changes sign as the temperature is increased along the triple line towards the critical end point temperature T_{cep} . This coefficient is given by Eq. (3.18) as

$$a(T) = (Q_\alpha - Q_\beta)(Q_\beta - Q_\gamma) \left[a_K + \frac{M_\alpha - M_\beta}{Q_\alpha - Q_\beta} \frac{M_\beta - M_\gamma}{Q_\beta - Q_\gamma} a_J + \left(\frac{M_\alpha - M_\beta}{Q_\alpha - Q_\beta} + \frac{M_\beta - M_\gamma}{Q_\beta - Q_\gamma} \right) a_C \right] \quad (3.25)$$

Before we proceed to investigate in what region of the parameter space the above two conditions are likely to be fulfilled, we first consider the restrictions on the parameter space implicit in our assumption that the bulk phase diagram of the binary liquid mixture is simple.

In general the phase diagram can be quite complicated.⁵⁰ However, in the special case that at low temperatures the two liquid phases have the same number density, a complete answer has been given by Furman *et al.*⁵¹ In Fig. 2 we have translated their results in our language. The topology of the bulk phase diagram depends on two dimensionless parameters: $(\bar{K} = \hat{K}/\hat{J}, \bar{C} = \hat{C}/\hat{J})$ or $(\bar{w}_{11}/\bar{w}_{12}, \bar{w}_{22}/\bar{w}_{12})$, where

$$\bar{w}_{ij} := - \int d^3r \tilde{w}_{ij}(\mathbf{r}). \quad (3.26)$$

\hat{J} or \bar{w}_{12} , respectively, define the temperature scale. The region in which the phase diagram is simple is given by

$$|\bar{C}| < \min\{0.28(\bar{K} + 3), (\bar{K} - 3)/2\}, \quad (3.27a)$$

$$\hat{J} > 0, \quad \bar{K} > 3.80. \quad (3.27b)$$

In terms of the interaction parameters \bar{w}_{ij} we have

$$\bar{w}_{11}/\bar{w}_{12} < 2, \quad \bar{w}_{22}/\bar{w}_{12} < 2, \quad (3.28a)$$

$$\bar{w}_{11}/\bar{w}_{12} + \bar{w}_{22}/\bar{w}_{12} > 2, \quad (3.28b)$$

$$0.29(\bar{w}_{11}/\bar{w}_{12} + \bar{w}_{22}/\bar{w}_{12}) < 1, \quad (3.28c)$$

and

$$0.11(\bar{w}_{11}/\bar{w}_{12} + \bar{w}_{22}/\bar{w}_{12}) + 1.79 \min\{\bar{w}_{11}/\bar{w}_{12}, \bar{w}_{22}/\bar{w}_{12}\} > 1. \quad (3.28d)$$

A common choice for $\tilde{w}_{ij}(r)$ is

$$\tilde{w}_{ij}(\mathbf{r}) = \begin{cases} 4\epsilon_{ij}[(\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^6], & r/\sigma_{ij} \geq 2^{1/6} \\ -\epsilon_{ij}, & r/\sigma_{ij} < 2^{1/6}. \end{cases} \quad (3.29)$$

With this choice one finds, that

$$\frac{t_{3,ij}}{t_{3,12}} = \frac{\bar{w}_{ij}}{\bar{w}_{12}} \left(\frac{\sigma_{ij}}{\sigma_{12}} \right)^3. \quad (3.30)$$

Equations (3.27)–(3.30) show that in the case of equal core sizes ($\sigma_{ij} = \sigma_{12}$) the axes in Fig. 2(a) can be relabeled by

$$(\bar{K}, \bar{C}) \leftrightarrow (a_K/a_J, a_C/a_J)$$

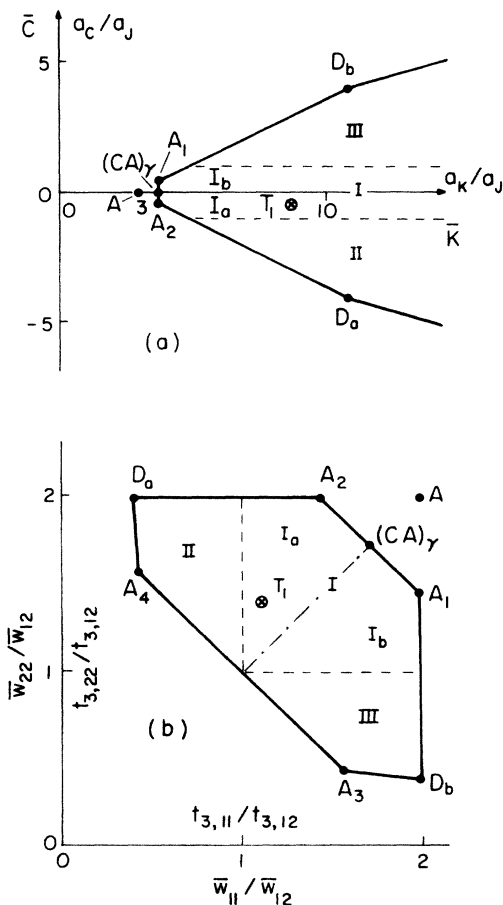


FIG. 2. Accessible interaction parameters for simple binary liquid mixtures expressed in terms of (a) (\bar{K}, \bar{C}) and (b) $(\bar{w}_{11}/\bar{w}_{12}, \bar{w}_{22}/\bar{w}_{12})$. Apart from small portions the enclosed areas are given by the region P_γ in Fig. 3 of Ref. 51. The triangle AA_1A_2 includes the so-called "shield" region (Ref. 51) and has therefore to be omitted. $(CA)_\gamma$, D_a , and D_b denote the same points as in Fig. 3 of Ref. 51. A is the symmetry point of Fig. 3 in Ref. 51. $\overline{A_1D_b}$ ($\overline{A_2D_a}$) represents a part of C_b (C_a) and $\overline{D_bA_3}$ ($\overline{D_aA_4}$) mimics the separatrix between P_γ and $P_{b\gamma}$ ($P_{a\gamma}$) in Fig. 3 of Ref. 51. The line $\overline{A_3A_4}$ in (b) stems from the condition $\hat{J} > 0$. T_1 denotes the locus of the calculation by Tarazona *et al.* (Refs. 4 and 52) (see the appendix). The calculation of Telo da Gama and Evans in Ref. 53, T_2 , is very close to T_1 . The coordinates of the various points are (a) $A = (3, 0)$, $(CA)_\gamma = (3.80, 0)$, $D_{a(b)} = [10.8, -(+)3.90]$, $A_{1(2)} = [3.80, +(-)0.40]$, $T_1 = (8.82, -0.47)$, $T_2 = (8.82, -0.36)$, and in (b) $A = (2, 2)$, $(CA)_\gamma = (1.73, 1.73)$, $D_a = (0.41, 2)$, $A_2 = (1.45, 2)$, $A_4 = (0.44, 1.56)$, $T_1 = (1.14, 1.38)$, $T_2 = (1.16, 1.35)$. The other points are given by symmetry. For further explanations see the main text.

and in Fig. 2(b) by

$$(\bar{w}_{11}/\bar{w}_{12}, \bar{w}_{22}/\bar{w}_{12}) \leftrightarrow (t_{3,11}/t_{3,12}, t_{3,22}/t_{3,12}).$$

This equivalence is certainly not true for arbitrary potentials, but we think it is reasonable to assume that for potentials of interest the parameters which enter the conditions for the separatrix [Eqs. (3.24) and (3.25)] can vary only within the regions indicated in Fig. 2 (recall that $A \equiv 1$, $B \equiv 2$). Having determined the restrictions on the parameters implicit in the assumption of a simple phase diagram, we return to the implications of the requirements for critical wetting that $a(T)$ be negative at low temperatures and positive at the critical end point temperature. We consider the former condition first.

According to the discussion preceding Eq. (3.24) the condition that $a(T)$ be negative at low temperatures is that the inequality of (3.24) be satisfied. With the restriction of equal hard-core radii, this inequality is fulfilled in all but region III of Fig. 2. In that region, the system is either wet at low temperatures, and so undergoes no wetting transition, or it undergoes a first-order wetting transition. (If the roles of A and B are reversed, then these statements apply to region II.) Thus this condition for a critical wetting is always satisfied in region I, is satisfied in region II if the triple line is approached from the A -rich liquid phase, and is satisfied in region III if approached from the B -rich side.

Just which region a given system is in is easily determined if the molecules have similar hard-core radii. In this case the more attractive molecules dominate the composition of the critical fluid, $M_c = \rho_{1,c} - \rho_{2,c}$. (This is in agreement with the numerical results in Refs. 4, 52, and 53.) This means that the experimentally known sign of M_c determines the sign of \bar{C} :

$$M_c \geq 0 \leftrightarrow \bar{C} \geq 0. \quad (3.31)$$

Along the same line of arguments as given above, we expect that this can be converted to a similar statement concerning the interaction strengths:

$$M_c \geq 0 \leftrightarrow t_{3,11} \geq t_{3,22}. \quad (3.32)$$

Thus, if the experimentally known value of the critical concentration is negative, the system is above the main diagonal. This, together with the results of the preceding paragraphs implies the following: in a system in which the bulk critical fluid is strongly dominated by A atoms, critical wetting can only be observed when the triple line is approached from the B -rich liquid side and vice versa. If the critical fluid is only weakly dominated by one of the two components (i.e., the system lies in region I) the vapor is not wetted by either of the two components at low temperatures. We emphasize that these crude rules are based on the assumption of similar core radii. The effect of different core sizes must be checked separately.

Our remaining task is to determine under what conditions $a(T_{cep})$ will be positive. We assume that if this is so, a wetting transition will have taken place. (It is conceivable that even at T_{cep} Ω_r has only a local minimum at $l = \infty$, whereas the global minimum remains at a finite

value of l so that the system does not wet the vapor. Such a behavior would be enforced by strong interactions at short distances, and we do not consider it here.) To discuss this question, we return to Eq. (3.25). We introduce the following three functions:

$$\lambda_{\alpha\beta} \left(\frac{\bar{w}_{11}}{\bar{w}_{12}}, \frac{\bar{w}_{22}}{\bar{w}_{12}} \right) = \frac{M_\alpha - M_\beta}{Q_\alpha - Q_\beta} \Big|_{T=T_{\text{cep}}}, \quad (3.33a)$$

$$\lambda_{\beta\gamma} \left(\frac{\bar{w}_{11}}{\bar{w}_{12}}, \frac{\bar{w}_{22}}{\bar{w}_{12}} \right) = \frac{M_\beta - M_\gamma}{Q_\beta - Q_\beta} \Big|_{T=T_{\text{cep}}}. \quad (3.33b)$$

$\lambda_{\alpha\beta}$ is independent of whether α or β is the A -rich liquid phase, whereas the $\lambda_{\beta\gamma}$ are two different functions according to whether β is the A -rich or B -rich liquid phase. Because the ratios on the right-hand sides of Eqs. (3.33) are evaluated at the critical end point, $\lambda_{\alpha\beta}$ and $\lambda_{\beta\gamma}$ depend

only on the variables which determine the bulk phase diagram. Note that by approaching the critical end point from below along the triple line, $M_\alpha - M_\beta \sim \kappa_1 \tau^\beta$ and $Q_\alpha - Q_\beta \sim \kappa_2 \tau^\beta$, where $\tau = (T_{\text{cep}} - T)/T_{\text{cep}}$ and $\beta = 0.5$ in MFT. Therefore, $\lambda_{\alpha\beta}$ is equal to the ratio of the amplitudes κ_1/κ_2 . Due to $|M| \leq Q$ and due to the low density of the gas phase γ one has

$$\lambda_{\beta\gamma} \cong M_c/Q_c, \quad |\lambda_{\beta\gamma}| < 1. \quad (3.34)$$

M_c and Q_c are the concentration and overall density, respectively, of the critical fluid. In the case $\bar{w}_{11} = \bar{w}_{22}$ and equal core sizes one has $M_c = 0$ and then $\lambda_{\beta\gamma} \cong -M_{\gamma,c}/Q_c$; $M_{\gamma,c}$ is the concentration of the gas phase at T_{cep} . In this case $|\lambda_{\beta\gamma}| \ll 1$.

The condition $a(T_{\text{cep}}) > 0$ must be formulated separately for various cases.

For case I, if $Q_\alpha \geq Q_\beta$ and $M_\alpha \geq M_\beta$, then

$$\frac{t_{3,11}}{t_{3,12}} \geq \frac{-1}{(1 + \lambda_{\alpha\beta})(1 + \lambda_{\beta\gamma})} [2(1 - \lambda_{\alpha\beta}\lambda_{\beta\gamma}) + (1 - \lambda_{\alpha\beta})(1 - \lambda_{\beta\gamma})t_{3,22}/t_{3,12}]. \quad (3.35a)$$

For case II, if $Q_\alpha \geq Q_\beta$ and $M_\alpha \leq M_\beta$, then

$$\frac{t_{3,22}}{t_{3,12}} \geq \frac{-1}{(1 - \lambda_{\alpha\beta})(1 - \lambda_{\beta\gamma})} [2(1 - \lambda_{\alpha\beta}\lambda_{\beta\gamma}) + (1 + \lambda_{\alpha\beta})(1 + \lambda_{\beta\gamma})t_{3,11}/t_{3,12}]. \quad (3.35b)$$

In Eqs. (3.35) the upper (lower) inequality signs belong together. Each of these two cases must be studied in the case that α is the A -rich or B -rich liquid phase. The general procedure is now obvious. Taking into account Eq. (3.30), one starts with, say, the situation depicted in Fig. 1(b). Then the overlap between the regions defined by Eq. (3.24) and Eq. (3.35) gives within the allowed area of Fig. 2(b) the loci of systems which fulfill the necessary conditions for critical wetting. Then these systems have to be investigated further with respect to the next-to-leading-order terms of their interaction potentials. This procedure must be repeated for the case that the α phase is the B -rich liquid phase. As an input one has to determine the functions $\lambda_{\alpha\beta}$ and $\lambda_{\beta\gamma}$. This requires a substantial numerical effort, especially to include the effect of different hard-core radii. This is the subject of further research.⁵⁴ Here we adopt a simpler point of view. These functions $\lambda_{\alpha\beta}$ and $\lambda_{\beta\gamma}$ are purely bulk properties of binary liquid mixtures, and it should be relatively easy to determine them from bulk density and concentration measurements. Therefore, we regard these functions as known, and we give some conditions which are especially favorable for critical wetting. This discussion uses the fact that we have always $1 \pm \lambda_{\beta\gamma} > 0$ [see Eq. (3.34)] and that $\lambda_{\alpha\beta} > 0$ (< 0) in case I (II). The most promising situation in case I is to have $Q_\alpha > Q_\beta$ and $M_\alpha > M_\beta$. Then the corresponding upper inequality in Eq. (3.35a) is automatically fulfilled if the expression in the square brackets is positive.

If $Q_\alpha > Q_\beta$, $M_\alpha > M_\beta$, $0 \leq \lambda_{\alpha\beta} < 1$, then

$$\frac{t_{3,22}}{t_{3,12}} > \frac{2(\lambda_{\alpha\beta}\lambda_{\beta\gamma} - 1)}{(1 - \lambda_{\alpha\beta})(1 - \lambda_{\beta\gamma})} \quad (3.36)$$

guarantees that the upper inequality of Eq. (3.35a) is fulfilled and is a simpler condition. Equation (3.36) is fulfilled for $\lambda_{\beta\gamma} < \lambda_{\alpha\beta}^{-1}$ and for the stronger inequality $\lambda_{\beta\gamma} < 0$, i.e., $M_c < 0$. For $Q_\alpha > Q_\beta$, $M_\alpha > M_\beta$, and $\lambda_{\alpha\beta} = 1$ we need $\lambda_{\beta\gamma} < 1$ which is true for $M_c < 0$.

If $Q_\alpha > Q_\beta$, $M_\alpha > M_\beta$, $\lambda_{\alpha\beta} > 1$, then

$$\frac{t_{3,22}}{t_{3,12}} < \frac{2(\lambda_{\alpha\beta}\lambda_{\beta\gamma} - 1)}{(1 - \lambda_{\alpha\beta})(1 - \lambda_{\beta\gamma})}. \quad (3.37)$$

Here, contrary to Eq. (3.36), $\lambda_{\beta\gamma} < \lambda_{\alpha\beta}^{-1}$ or $M_c < 0$ is only a necessary, but not sufficient, condition to fulfill Eq. (3.37). In summary, $Q_\alpha > Q_\beta$, $M_\alpha > M_\beta$, $\lambda_{\alpha\beta} \leq 1$, $M_c < 0$ is a sufficient condition to have a wetting transition.

In case II the most promising situation is $Q_\alpha > Q_\beta$, $M_\alpha < M_\beta$. Again a sufficient condition for Eq. (3.35b) is that the quantity in the square brackets in Eq. (3.35b) is positive.

If $Q_\alpha > Q_\beta$, $M_\alpha < M_\beta$, $-1 < \lambda_{\alpha\beta} \leq 0$, then

$$\frac{t_{3,11}}{t_{3,12}} > \frac{2(\lambda_{\alpha\beta}\lambda_{\beta\gamma} - 1)}{(1 + \lambda_{\alpha\beta})(1 + \lambda_{\beta\gamma})} \quad (3.38)$$

guarantees that the upper inequality of (3.35b) is fulfilled and is a simpler condition. Equation (3.38) is satisfied for $\lambda_{\beta\gamma} > \lambda_{\alpha\beta}^{-1}$ and for the stronger inequality $\lambda_{\beta\gamma} > 0$, i.e., $M_c > 0$. For $\lambda_{\alpha\beta} = -1$ we need $\lambda_{\beta\gamma} > -1$ which is true for $M_c > 0$. Finally, if $Q_\alpha > Q_\beta$, $M_\alpha < M_\beta$, $\lambda_{\alpha\beta} < -1$, then

$$\frac{t_{3,11}}{t_{3,12}} < \frac{2(\lambda_{\alpha\beta}\lambda_{\beta\gamma} - 1)}{(1 + \lambda_{\alpha\beta})(1 + \lambda_{\beta\gamma})} \quad (3.39)$$

is a sufficient condition for a wetting transition. Equation

(3.39) can only be satisfied if $\lambda_{\beta\gamma} > \lambda_{\alpha\beta}^{-1}$ which holds for $\lambda_{\beta\gamma} > 0$, i.e., $M_c > 0$. The considerations leading to Eqs. (3.36)–(3.39) can be summarized by giving the following conditions, either of which is sufficient for the existence of a wetting transition:

$$Q_\alpha > Q_\beta, M_\alpha > M_\beta, \lambda_{\alpha\beta} < 1, M_c < 0, \quad (3.40a)$$

$$Q_\alpha > Q_\beta, M_\alpha < M_\beta, -\lambda_{\alpha\beta} < 1, M_c > 0. \quad (3.40b)$$

Note especially that according to Eqs. (3.40) it is always favorable for a wetting transition that the intruding film (β) has the lower *number density*. For atoms with similar core radii we expect that liquid phase to have the larger (smaller) particle density which is rich in the more (less) attractive atoms:

$$Q_A \lesssim Q_B \leftrightarrow \bar{w}_{11} \lesssim \bar{w}_{22}. \quad (3.41)$$

Again, $Q_{A(B)}$ denotes the density of the A - (B -) rich liquid phase. We also expect the gas to be rich in the less attractive atoms. This is in agreement with the explicit calculations in Refs. 4 and 52. From Eqs. (3.40) and (3.41) we conclude that ordinarily a wetting transition takes place if the triple line is approached from the *less volatile* liquid phase (i.e., *higher* number density) and the wetting film is formed by the *more volatile* liquid phase (i.e., *lower* number density). As lower number densities are usually associated with higher mass densities, we expect heavier liquids to wet the interface between lighter liquids and their vapor.^{52,55} This is in fact found experimentally (see the discussion of the experiments at the end of Sec. V).

The regions of parameter space which permit a continuous wetting transition have now been deduced. If the intruding layer is B rich, the first requirement, that $a(T)$ be negative at low temperature so that an infinitely thick wetting layer corresponds to a *maximum* of the free energy and is thus unfavorable, is given by Eq. (3.24) which shows that the system should be located in regions I or II in Fig. 2. The second requirement, that $a(T_{cep})$ be posi-

tive so that an infinitely thick wetting layer corresponds to a *minimum* (assumed to be a global one) of the free energy, is given by Eq. (3.40) which, in conjunction with Eq. (3.41), shows that the system should be located in regions I_b or III. Therefore, region I_b satisfies both necessary conditions for critical wetting. If the intruding layer is A rich, then region I_a satisfies the necessary conditions for critical wetting.

Let us now assume that we have a system which satisfies the above necessary conditions for critical wetting. In that case the wetting transition is first order if $b(T_w) < 0$ and can be second order otherwise. To discuss the sign of $b(T_w)$ we introduce the following function:

$$\begin{aligned} \tilde{\lambda} & \left[\frac{t_{3,11}}{t_{3,12}}, \frac{t_{3,22}}{t_{3,12}}, \frac{\bar{w}_{11}}{\bar{w}_{12}}, \frac{\bar{w}_{22}}{\bar{w}_{12}} \right] \\ & = \frac{1}{2} \left[\frac{M_\alpha - M_\beta}{Q_\alpha - Q_\beta} + \frac{M_\beta - M_\gamma}{Q_\beta - Q_\gamma} \right] \Big|_{T_w}, \quad (3.42) \end{aligned}$$

where T_w is defined implicitly by $a(T_w) = 0$, i.e. [see Eq. (3.18)]:

$$\begin{aligned} \frac{t_{3,11}}{t_{3,12}} (1 + \Lambda_{\alpha\beta})(1 + \Lambda_{\beta\gamma}) + 2(1 - \Lambda_{\alpha\beta}\Lambda_{\beta\gamma}) \\ + \frac{t_{3,22}}{t_{3,12}} (1 - \Lambda_{\alpha\beta})(1 - \Lambda_{\beta\gamma}) = 0, \quad (3.43) \end{aligned}$$

where

$$\Lambda_{\alpha\beta} \left[\frac{T}{\bar{w}_{12}}, \frac{\bar{w}_{11}}{\bar{w}_{12}}, \frac{\bar{w}_{22}}{\bar{w}_{12}} \right] = \frac{M_\alpha - M_\beta}{Q_\alpha - Q_\beta}, \quad (3.44)$$

and a similar equation for $\Lambda_{\beta\gamma}$. Note that $\lambda_{\alpha\beta} = \Lambda_{\alpha\beta}(T_{cep})$ and that only in the case of critical wetting does T_w , defined by Eq. (3.43), actually coincide with the wetting temperature; for first-order wetting the transition occurs at a higher temperature. With Eqs. (3.18), (3.20), and (3.42)–(3.44) the condition for critical wetting is

$$\frac{t_{4,12}}{t_{3,12}} \left[1 + \frac{\tilde{\lambda} - 1}{2} \left[1 - \frac{t_{3,22}}{t_{3,11}} \right] \right] \geq \frac{t_{4,11}}{t_{3,11}} \left[1 + \frac{\tilde{\lambda} - 1}{2} \left[1 - \frac{t_{4,22}}{t_{4,11}} \right] + \frac{\tilde{\lambda}}{2} \left[\frac{t_{4,22}}{t_{4,11}} \frac{t_{3,11}}{t_{3,12}} - \frac{t_{3,22}}{t_{3,12}} \right] \right] \text{ for } Q_\alpha \geq Q_\beta. \quad (3.45)$$

Compared with the analogous condition in Eq. (2.20) for the one-component system near a wall, Eq. (3.45) shows that the existence of three independent interaction potentials already gives a quite complicated expression for the separatrix between first- and second-order wetting in binary fluid mixtures.

In MFT the relevant coordinates of a binary liquid mixture with respect to the order of wetting transitions in these systems form a 12-dimensional parameter space $\mathcal{P} = \{\bar{w}_{ij}; t_{3,ij}; t_{4,ij}; \sigma_{ij}\}$. The description of T_w for a first-order wetting transition and for the associated prewetting line requires an even larger parameter space because for these quantities the behavior of the interaction potentials at small distances is important. The same is true for multicritical wetting phenomena higher than tricritical. The description of critical wetting requires the smallest parameter space. The formulas derived above [Eqs. (3.24), (3.35), and (3.45)] give a general expression for the separatrix

$$\mathcal{S} = \left\{ (\bar{w}_{ij}; t_{3,ij}; t_{4,ij}; \sigma_{ij}) \in \mathcal{P} \mid F \left[\frac{\bar{w}_{11}}{\bar{w}_{12}}, \frac{\bar{w}_{22}}{\bar{w}_{12}}, \frac{t_{3,11}}{t_{3,12}}, \frac{t_{3,22}}{t_{3,12}}, \frac{t_{4,ij}}{t_{3,ij}}, \sigma_{ij} \right] = 0 \right\},$$

which divides \mathcal{P} into regions of first-order, second-order, and no wetting transition. \mathcal{S} is an 11-dimensional hypersurface, and F is given by Eqs. (3.24), (3.35), and (3.45) by replacing there the inequality signs by equality signs.

Tarazona *et al.*⁴ located numerically the one-dimensional intersection line between a two-dimensional⁵⁶ subspace of \mathcal{P} with \mathcal{S} . In the appendix we show that along that line the analytic expression for \mathcal{S} [Eqs. (3.24), (3.35), and

(3.45)] as derived by the sharp-kink approximation does agree with the numerical solution of the full MFE's. Furthermore, when the wetting transition is continuous we find that the condition $a(T_w)=0$ [see Eqs. (3.43) and (3.44)] yields the critical temperature which Tarazona *et al.* obtained. Thus, as in the case of a one-component fluid near a wall, we find once again that the sharp-kink approximation appears to give the same separatrix and critical wetting temperature as a full solution of the MFE's. This enhances our confidence in the expression for \mathcal{S} as given above for the whole parameter space \mathcal{P} . In such a large parameter space, it would be impossible to locate this separatrix numerically.

IV. BINARY LIQUID MIXTURE NEAR A WALL

In the preceding section we neglected the influence of the wall which contains the binary liquid mixture. We now focus just on this influence [see Fig. 1(c)] and its connection to the phenomena described in Sec. III. To provide a better understanding, the bulk phase diagram of a simple binary liquid mixture in the temperature, pressure, and chemical potential-difference space is shown schematically in Fig. 3. There are three bulk phases: the A -rich liquid (α), the B -rich liquid (β), and the vapor (γ). These phases are separated by two sheets of two-phase coexistence which meet at a triple line. The triple line ends at an upper critical end point T_{cep} . Figure 3 also displays the loci at which the surface free energy is singular. Each of the sheets of two-phase coexistence can exhibit its own line of singularities at which the interface between the wall and one phase is wetted by the other. Thus, in Fig. 3(a), the line of wetting transitions at which α wets the wall-vapor interface is denoted as l_1 . Similarly, l_2 is the line at which β wets the wall-vapor interface, and the line at which α wets the wall- β interface is denoted as l_3 . Each point of l_1 , l_2 , and l_3 represents a wetting transition which can be either first or second order. If it is first order, a prewetting line¹ is attached to such a point. Accordingly, the prewetting lines span the sheets S_1 , S_2 , and S_3 . These prewetting sheets also indicate at which side of the corresponding bulk coexistence sheet the surface free energy becomes singular. On the opposite side it is non-singular. Each prewetting sheet S_i starts to detach at a certain point P_i from its corresponding line of wetting transitions l_i indicating that the order of the wetting transition can change along that line. P_1 , P_2 , and P_3 are points of tricritical wetting transitions. A missing prewetting line indicates a second-order wetting transition. The prewetting sheets S_i meet the bulk coexistence sheets tangentially.⁵⁷ There is also, of course, the wetting phenomenon which was the subject of Sec. III, the wetting of the α -vapor interface by β [see Fig. 1(b)]. This occurs only on the triple line and is denoted as point W in Fig. 3(a). If this interfacial wetting transition happens to be first order, W is also associated with a prewetting line l_w . l_w lies in the bulk coexistence sheet which separates the α and γ phase and approaches the triple line again tangentially.

It is easy to show that, in Fig. 3(a), l_2 ends on the triple line at the temperature W . To see this we note that at

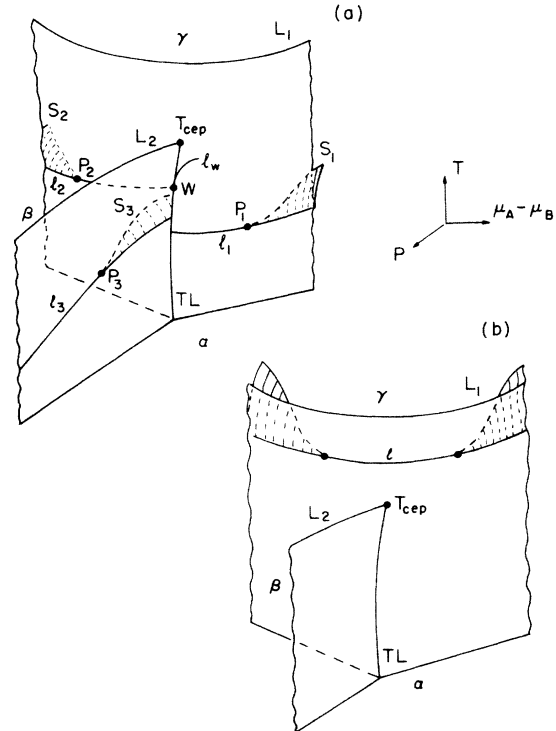


FIG. 3. Schematic phase diagram of a simple binary liquid mixture in the temperature (T), pressure (p), and chemical potential difference ($\mu_A - \mu_B$) space. α (β) is the A - (B -) rich liquid phase and γ is the vapor. L_1 (L_2) is the critical line which terminates the sheet of first-order bulk transitions between γ and $\alpha\beta$ (α and β). The triple line TL ends at the upper critical end point T_{cep} . As shown in (a), α wets the wall- γ interface along l_1 ; β wets the wall- γ interface along l_2 ; α wets the wall- β interface along l_3 , and β wets the α - γ interface at W with the corresponding prewetting line l_w . S_1 , S_2 , and S_3 are prewetting sheets and P_1 , P_2 , and P_3 denote the loci of multicritical wetting transitions. In (b) the $\alpha\beta$ fluid wets the wall- γ interface along l .

temperatures above that at which l_1 terminates at the triple line (and W is such a temperature)

$$\sigma_{w,\gamma} = \sigma_{w,\alpha} + \sigma_{\alpha,\gamma} \quad (4.1)$$

because α wets the wall- γ interface. Similarly, at temperatures above that at which l_3 terminates at the triple line (and W is such a temperature)

$$\sigma_{w,\beta} = \sigma_{w,\alpha} + \sigma_{\alpha,\beta} \quad (4.2)$$

because α wets the wall- β interface.

Because β does not wet the α - β interface below the temperature W ,

$$\sigma_{\alpha,\gamma} < \sigma_{\alpha,\beta} + \sigma_{\beta,\gamma}, \text{ below } W. \quad (4.3)$$

Equations (4.1)–(4.3) imply

$$\sigma_{w,\gamma} < \sigma_{w,\beta} + \sigma_{\beta,\gamma}, \text{ below } W. \quad (4.4)$$

Thus β does not wet the wall- γ interface on the triple line below W . By definition, then, the line l_2 must intersect the triple line at W or higher. Because β does wet the α - γ interface at and above W ,

$$\sigma_{\alpha,\gamma} = \sigma_{\alpha,\beta} + \sigma_{\beta,\gamma}, \quad \text{at and above } W, \quad (4.5)$$

which, with Eqs. (4.1) and (4.2), implies

$$\sigma_{w,\gamma} = \sigma_{w,\beta} + \sigma_{\beta,\gamma}, \quad \text{at and above } W. \quad (4.6)$$

This, then, identifies the point at which l_2 intersects the triple line as W itself.

Finally note that the end points of both l_1 and l_3 at the TL correspond to the wetting of the wall by the α phase. Within the sharp-kink approximation (see below) one can see, however, that these two wetting transitions on the triple line are not the same.

A consequence of the phase diagram of Fig. 3(a) is that the wall-vapor interface upon an increase in temperature is wetted in two stages along the triple line.³⁵ First, the wall-vapor interface is wetted by α . Then, at a higher

temperature, the α interface is wetted by β producing a wall- α - β -vapor interface.

If the wall potential is weakened, the wetting lines l_1 , l_3 , and l_2 increase in temperature, and their intersections with the triple line become closer as the difference between the α and β phase decreases. It is possible for these wetting temperatures to be above the critical end point temperature T_{cep} , in which case there is simply a line l of wetting transitions at which the one-phase fluid wets the wall-vapor interface.³⁵ The phase diagram is then as in Fig. 3(b). Again there can be prewetting sheets. It is easy to imagine that the two situations of Fig. 3(a) and (b) do not exhaust all possibilities.³⁵

In the remainder of this section we shall discuss these wetting transitions near the wall within the sharp-kink approximation along the same lines as in Secs. II and III. We begin with the free-energy functional

$$\begin{aligned} \Omega[\{\rho_i\}] = & \int d^3r f_h[\{\rho_i(\mathbf{r})\}] + \frac{1}{2} \sum_{i,j} \int d^3r \int d^3r' \tilde{w}_{ij}(|\mathbf{r}-\mathbf{r}'|) \rho_i(\mathbf{r}) \rho_j(\mathbf{r}') \\ & + \sum_i \int d^3r V_i(\mathbf{r}) \rho_i(\mathbf{r}) \rho_w - \sum_i \mu_i \int d^3r \rho_i(\mathbf{r}). \end{aligned} \quad (4.7)$$

Compared to Eq. (3.2) we added the interaction $V_i(\mathbf{r})\rho_w$ between particles of species $i=1(\equiv A)$, $2(\equiv B)$, and the wall with a mean number density ρ_w . Without loss of generality we shall focus on the wetting of the wall- β interface by α , i.e., l_3 in Fig. 3(a) [see also Fig. 1(c)]. Within the sharp-kink approximation we seek to minimize Eq. (4.7) with the ansatz

$$\rho_i(\mathbf{r}) = \begin{cases} \rho_{i,\alpha}, & d_w^{(i)} \leq z \leq l \\ \rho_{i,\beta}, & l < z \leq L \\ 0, & \text{otherwise.} \end{cases} \quad (4.8)$$

Equation (4.8) is a generalization of Eq. (2.2). Note that we allow for two different excluded volumina $d_w^{(i)}$ for the two species. Inserting Eq. (4.8) into Eq. (4.7) we obtain (A denotes the surface area)

$$\Omega[\{\rho_i\}] = AL\Omega_b(\rho_{i,\beta}) + A\Omega_s(l), \quad (4.9)$$

where

$$\begin{aligned} \Omega_b(\rho_{i,\beta}) = & f_h(\rho_{1,\beta}, \rho_{2,\beta}) \\ & + \frac{1}{2} \sum_{i,j} \rho_{i,\beta} \rho_{j,\beta} \int_{-\infty}^{\infty} dx w_{ij}(|x|) \\ & - \sum_i \mu_i \rho_{i,\beta} \end{aligned} \quad (4.10)$$

and $w_{ij}(x)$ is defined in analogy to Eq. (2.5). The surface contribution can be written as

$$\begin{aligned} \Omega_s(l) = & \sigma_{\beta,\text{vac}} + l[\Omega_b(\rho_{i,\alpha}) - \Omega_b(\rho_{i,\beta})] \\ & + \sigma_{\alpha,\beta} + \sigma_{\alpha,w} + \omega(l). \end{aligned} \quad (4.11)$$

The first term is the energy required to terminate the β phase at the surface of convenience $z=L$,

$$\sigma_{\beta,\text{vac}} = -\frac{1}{2} \sum_{i,j} \rho_{i,\beta} \rho_{j,\beta} \int_0^{\infty} dy t_{ij}(y), \quad (4.12)$$

with $t_{ij}(y)$ given by Eq. (3.13). The second term is the cost of free energy for being off α - β coexistence. The third term describes the surface tension between the α and β phase

$$\sigma_{\alpha,\beta} = -\frac{1}{2} \sum_{i,j} (\rho_{i,\alpha} - \rho_{i,\beta})(\rho_{j,\alpha} - \rho_{j,\beta}) \int_0^{\infty} dy t_{ij}(y). \quad (4.13)$$

The fourth term is the surface free energy between the wall and the α phase if the α - β coexistence would be approached from the α side:

$$\begin{aligned} \sigma_{\alpha,w} = & -\frac{1}{2} \sum_{i,j} d_{ij} \rho_{i,\alpha} \rho_{j,\alpha} \int_{-\infty}^{\infty} dx w_{ij}(|x|) + \sum_i d_w^{(i)} \mu_i \rho_{i,\alpha} + \sum_i \rho_{i,\alpha} \rho_w \int_{d_w^{(i)}}^{\infty} dz V_i(z) + \rho_{1,\alpha} \rho_{2,\alpha} \int_0^{d|} dy t_{12}(y) \\ & + |d/2| \{f_h(\rho_{1,\alpha}; 0) + f_h(0; \rho_{2,\alpha}) + [2\theta(d) - 1][f_h(0; \rho_{2,\alpha}) - f_h(\rho_{1,\alpha}; 0)]\} - d_{ij} f_h(\rho_{1,\alpha}; \rho_{2,\alpha}) + \sigma_{\alpha,\text{vac}}, \end{aligned} \quad (4.14)$$

where

$$d_{ij} = \max\{d_w^{(1)}, d_w^{(2)}\}, \quad d = d_w^{(1)} - d_w^{(2)}, \quad (4.15)$$

and $\theta(d)$ is the Heaviside function. The final contribution to Eq. (4.11) represents the correction to the above due to the finite thickness of the α film

$$\omega(l) = \sum_{i,j} (\rho_{i,\alpha} - \rho_{i,\beta}) \left[\rho_{j,\alpha} \int_{l-d_w^{(j)}}^{\infty} dy t_{ij}(y) - \delta_{ij} \rho_w \int_l^{\infty} dz V_j(z) \right], \quad (4.16)$$

where δ_{ij} is the Kronecker δ function. With the expansion

$$V_i(z) = -(u_{3,i} z^{-3} + u_{4,i} z^{-4} + \dots), \quad (4.17)$$

$\omega(l)$ takes the form, for large l ,

$$\omega(l) = al^{-2} + bl^{-3}, \quad (4.18)$$

where

$$a = \frac{1}{2} \sum_{i,j} (\rho_{i,\alpha} - \rho_{i,\beta}) (\rho_w u_{3,j} \delta_{ij} - \rho_{j,\alpha} t_{3,ij}) \quad (4.19)$$

and

$$b = \frac{1}{3} \sum_{i,j} (\rho_{i,\alpha} - \rho_{i,\beta}) [\rho_w u_{4,j} \delta_{ij} - \rho_{j,\alpha} (t_{4,ij} + 3d_w^{(j)} t_{3,ij})]. \quad (4.20)$$

$t_{3,ij}$ and $t_{4,ij}$ are given by Eq. (3.16). The temperature dependence of a and b can be more easily understood in terms of the variables M, Q as defined in Eq. (3.4):

$$a = \frac{1}{4} (Q_\alpha - Q_\beta) a_+ + \frac{1}{4} (M_\alpha - M_\beta) a_-, \quad (4.21a)$$

where

$$a_\pm = \rho_w (u_{3,1} \pm u_{3,2}) - \frac{1}{2} \left\{ \begin{matrix} M_\alpha \\ Q_\alpha \end{matrix} \right\} (t_{3,11} - t_{3,22}) - \frac{1}{2} \left\{ \begin{matrix} Q_\alpha \\ M_\alpha \end{matrix} \right\} (t_{3,11} \pm 2t_{3,12} + t_{3,22}), \quad (4.21b)$$

and

$$b = \frac{1}{6} (Q_\alpha - Q_\beta) b_+ + \frac{1}{6} (M_\alpha - M_\beta) b_-, \quad (4.22a)$$

where

$$b_\pm = \rho_w (u_{4,1} \pm u_{4,2}) - \frac{1}{2} \left\{ \begin{matrix} M_\alpha \\ Q_\alpha \end{matrix} \right\} \hat{b}_\pm - \frac{1}{2} \left\{ \begin{matrix} Q_\alpha \\ M_\beta \end{matrix} \right\} \tilde{b}_\pm, \quad (4.22b)$$

with

$$\hat{b}_\pm = t_{4,11} - t_{4,22} + 3(d_w^{(1)} t_{3,11} - d_w^{(2)} t_{3,22} \pm dt_{3,12}) \quad (4.22c)$$

and

$$\tilde{b}_\pm = t_{4,11} \pm 2t_{4,12} + t_{4,22} + 3[d_w^{(1)} t_{3,11} + d_w^{(2)} t_{3,22} \pm (d_w^{(1)} + d_w^{(2)}) t_{3,12}]. \quad (4.22d)$$

The most transparent conclusions which can be drawn

from Eqs. (4.19)–(4.22) concern the necessary condition $a(T=0) < 0$ for critical wetting [see Fig. 3(a)]:

$$\frac{u_{3,A}}{t_{3,AA}} < \frac{\rho_0^{(A)}}{\rho_w} \quad (\text{along } l_1), \quad (4.23a)$$

$$\frac{u_{3,B}}{t_{3,BB}} < \frac{\rho_0^{(B)}}{\rho_w} \quad (\text{along } l_2), \quad (4.23b)$$

$$\frac{u_{3,A}}{t_{3,AA}} \left[1 - \frac{u_{3,B}}{u_{3,A}} \frac{\rho_0^{(B)}}{\rho_0^{(A)}} \right] < \frac{\rho_0^{(A)}}{\rho_w} \left[1 - \frac{t_{3,AB}}{t_{3,AA}} \frac{\rho_0^{(B)}}{\rho_0^{(A)}} \right] \quad (\text{along } l_3). \quad (4.23c)$$

Equations (4.23a) and (4.23b) are more likely fulfilled if $\rho_0^{(A)}$ and $\rho_0^{(B)}$, respectively, are large which will be the case if the pressure p is high. If one goes away from the triple line along l_1 or l_2 the pressure decreases, and therefore Eqs. (4.23a) and (4.23b) can be violated on that way. Therefore, the trend towards first-order wetting increases in these directions as indicated in Fig. 3(a). If one moves at low temperature on the coexistence sheet between the α and the β phase away from the triple line the pressure increases and so do $\rho_0^{(A)}$ and $\rho_0^{(B)}$. In the case that their ratio $\rho_0^{(B)}/\rho_0^{(A)}$ remains fairly constant, the right-hand side of Eq. (4.23c) will increase in that direction enhancing the possibility for critical wetting. Along l_3 this trend again is indicated in Fig. 3(a). Therefore, for a binary liquid mixture the critical wetting of the wall-vapor (wall-liquid) interface is more likely to occur close to (away from) the triple line.

In the case of critical wetting the transition temperature T_W is given by $a(T=T_W)=0$. Equation (4.19) shows that $\rho_j(T_W) \sim u_{3,j}/t_{3,ij}$. For a weak substrate, $\rho_j(T_W)$ is small, and therefore T_W is high. This is the same trend as in the case of a one-component system near a wall and leads to the representation in Fig. 3(b).

Finally, let us come back to the relative position of the two end points of l_1 and l_3 at the triple line. In both cases the wall is wetted by α . Let us assume now the situation—different from Fig. 3(a)—that at both end points critical wetting occurs. Then, as just stated, their loci are determined by $a(T)=0$. If we neglect along l_1 the vapor densities compared to the liquid densities and in the A -rich liquid the density of B - particles compared to the density of A particles this condition leads to

$$\rho_{A,\alpha}(T_W)/\rho_w \cong u_{3,A}/t_{3,AA} \quad (\text{along } l_1). \quad (4.24a)$$

If we neglect along l_3 as above in the A - (B -) rich phase the density of the B - (A -) particles compared to the density of the A - (B -) particles we arrive at

$$\rho_{A,\alpha}(T_W)/\rho_w \cong (u_{3,A} - \hat{\gamma} u_{3,B}) / (t_{3,AA} - \hat{\gamma} t_{3,BA}) \quad (\text{along } l_3), \quad (4.24b)$$

where $\hat{\gamma} = (\sigma_{AA}/\sigma_{BB})^3$. Similar arguments give for l_2

$$\rho_{B,\beta}(T_W)/\rho_w \cong u_{3,B}/t_{3,BB} \quad (\text{along } l_2). \quad (4.24c)$$

Along the triple line the two other arguments of $\rho_{A,\alpha}$, namely the pressure and the chemical potential difference,

do not vary much so that at the triple line $\rho_{A,\alpha}$ practically depends only on T . So the different right-hand sides in Eqs. (4.24a) and (4.24b) lead indeed to different end points of l_1 and l_3 .

Among the systems with $a(T=0) < 0$ only those will undergo a wetting transition for which a goes to zero at some higher temperature. For l_3 this means that if we start at a certain point on the bottom of the α - β coexistence sheet we must require that along a line of constant pressure in this sheet a has to become zero at least at the intersection of this line with the critical line L_2 in Fig. 3(a). The corresponding condition for l_1 (l_2) is somewhat ambiguous but a sufficient one would be that starting at the bottom of the $\alpha\gamma$ - ($\beta\gamma$ -) coexistence sheet along a line of constant chemical potential difference a must become zero at least at the intersection of this line with the plane $T = T_{\text{cep}}$. Then critical wetting will occur if $b(T_w) > 0$. To have a wetting transition line like l in Fig. 3(b) we must have $a(T) < 0$ for all $T < T_{\text{cep}}$ and a becoming zero along a line of constant chemical potential difference at least at the critical line L_1 . Given the expression for a and b in Eqs. (4.21) and (4.22) this results in rather complex expressions for the various separatrices between first- and second-order wetting transitions. We refrain from discussing them and refer to the general trends as described above.

V. SUMMARY

The sharp-kink approximation has been used to calculate surface quantities within the framework of mean-field theory which in the experimentally relevant case of three-dimensional systems with long-range forces will yield the correct critical exponents for critical wetting.^{15,16,19} Within the sharp-kink approximation, the smooth variation of all densities between the values appropriate to the bulk phase on one side of an interface to those appropriate to the bulk phase on the other is replaced by a discontinuous jump between these bulk values. The only parameter which is varied in order to minimize the surface free energy is the thickness l of a film of a third phase which interposes itself between the two bulk phases. We have seen that in all cases in which the full inhomogeneous mean-field equations were solved and which resulted in smooth density profiles, the results for the transition temperature of critical wetting and for the location of the separatrix between critical and first-order wetting was the same as that obtained from the sharp-kink approximation. Because these quantities depend on the first two terms of the thick-film expansion of the surface free energy $\omega(l)$, of order al^{-2} and bl^{-3} , respectively, we are led to believe that the effect of the smooth profile must only appear in higher order. Indeed, the authors of Ref. 16 find that, in a low-temperature-series approximation, the effect of the profile appears first in order l^{-5} .

Therefore, within mean-field theory the location of the separatrix between first- and second-order wetting transitions and the transition temperature of critical wetting are given by analytic expressions in terms of the bulk densities of the coexisting phases and the first two leading terms of the interaction potentials of the particles. These

expressions can then be used to predict general trends in such diverse systems as one-component fluids near a wall, binary liquid mixtures near a wall, and binary liquid mixtures at three-phase coexistence. Furthermore, these general analytic expressions demonstrate explicitly that the wetting phenomena are examples, in which details of the microscopic interaction potentials—like their next-to-leading-order terms at large distances—manifest themselves in a macroscopic effect, namely whether the coverage of a substrate increases continuously or discontinuously upon a rise in temperature. This, however, makes it very difficult to make a precise prediction for a specific experiment. Given the knowledge of the bulk densities, from experimental data for example, one has to determine precisely the interaction potentials. This problem represents a wide field of research of its own and we refrain from discussing it. Reference 58 can serve as a recent guide through the corresponding literature. The effect of retardation of the van der Waals forces, however, requires some additional remarks. At distances larger than $r_0^{(i)} = c/v_0^{(i)}$, where $v_0^{(i)}$ is the dominant absorption frequency of the particle i in the ultraviolet, \tilde{w}_i is proportional to r^{-7} instead of r^{-6} . This leads to a behavior $\omega(l) \sim l^{-3}$ for $l \gg r_0$. This has been confirmed by the experiments of Sabisky and Anderson⁵⁹ and of Kayser *et al.*⁶⁰ in which they found a quantitative agreement with the theory of Dzyaloshinskii *et al.*⁶¹ From that we draw three conclusions. First, the coefficient a describing the leading asymptotic behavior of $\omega(l)$ is l dependent. This l dependence becomes important for l in the order of several hundred angstroms, such that a vanishes proportional to r_0/l . Note, however, that in the case of critical wetting the thickness of the wetting film grows *linearly* by approaching the wetting transition temperature in *both* regimes, $l/r_0 \ll 1$ and $l/r_0 \gg 1$, because the corresponding critical exponent depends only on the difference between the exponent of the leading- and next-to-leading-order term in $\omega(l)$,¹¹ and there should be correction terms in both regimes. The critical exponent of the diverging parallel correlation length, however, changes from 2.5 for $l \ll r_0$ to 3 for $l \gg r_0$.¹¹ Second, the quantitative agreement between experiment^{59,60} and theory⁶¹ indicates that at least the leading asymptotic behavior of ω , i.e., a , can be estimated quite accurately once the frequencies $v_0^{(i)}$ are known. From the sign of a at low temperatures alone one can deduce significant information. If it is positive, the system is expected to be either always wet, and thus undergoes no wetting transition, or to undergo a first-order wetting transition. If a is negative at low temperatures, a critical wetting is not ruled out, and one must then address the far more difficult task of determining the sign of the coefficient of the next-to-leading-order term, b , at the temperature at which critical wetting could take place. As we have argued in Sec. II, this coefficient depends *inter alia* on the structural details of the substrate. Our third conclusion concerns the binary liquid mixtures. There it is quite possible that, for example, $r_0^{(1)}$ is much larger than $r_0^{(2)}$ due to different absorption spectra of the two molecules. Because a and b depend on linear combinations of the potential parameters of molecules 1 and 2 [see Eqs. (3.18)–(3.20)] this constellation means that, for

$r_0^{(2)} \ll l \ll r_0^{(1)}$, a depends only on $t_{3,11}$, whereas the leading, retarded part of molecule 2 contributes to b .

Finally, we want to discuss briefly the experiments which are connected to our theoretical work. The wetting phenomena of a one-component system near a wall have been reviewed recently by Bienfait.⁶² Surprisingly, out of a large number of experiments only a few wetting transitions have been reported. Along its sublimation curve carbon tetrafluoride adsorbed on graphite displays a first-order wetting transition.^{63,64} ^4He adsorbed on copper exhibits wetting transitions when the melting line is approached from the liquid side. Carmi *et al.*⁶⁵ report a continuous wetting transition in the case that the ^4He crystals grow in their [0001] direction perpendicular to the substrate and a first-order wetting transition if the ^4He crystals grow along their [10 $\bar{1}$ 0] direction perpendicular to the substrate. This sensitivity of the order of the wetting transition on the growth direction agrees with our findings. A different crystallographic orientation of the adsorbate with respect to the substrate results in a change of the potential parameter t_4^{latt} in Eq. (2.26) and can bring about a change in the order of the wetting transition. However, as already pointed out, one must be cautious in applying directly our results to the melting curve. Along the gas-liquid coexistence line, where our calculations should work best, only two wetting transitions have been found recently: liquid ^4He adsorbed on gold and on silver.⁶⁶ However, the outcome of these experiments is not yet quite understood. First, it is not obvious why ^4He does not wet the very attractive Au and Ag substrate. The formation of a few layers of solid ^4He next to the substrate may be important for this finding.⁶⁷ Second, the coefficient a is about certainly positive at low temperatures so that a first-order wetting would be expected.⁶⁸ Yet a continuous growth of layer thickness consistent with $l \sim (T_w - T)^{-1}$ which is expected for critical wetting¹⁵ is observed up to thick films. Third, if a wetting transition occurs, its temperature appears to be 10 mK off the He liquid-gas critical temperature which is certainly surprising. So, to the best of our knowledge up to now, no clear cut transition at gas-liquid coexistence for the wetting of a substrate, neither first- nor second-order, has been reported recently.⁶⁹ In all the other experiments either the substrate is already wet at low temperatures or the wetting transition along gas-liquid coexistence is preempted by the triple point (see for example Krim *et al.*⁷⁰) or higher temperatures have not yet been studied systematically.

In the case of binary liquid mixtures we are aware of three systems in which a transition of the wetting of the vapor phase has been reported: methanol-cyclohexane,⁷¹ isopropanol-perfluormethylcyclohexane,^{72,73} and cyclohexane-acetonitrile.⁷⁴ Only in the second example have strong efforts been made to determine the order of the transition, and it was found to be first order.^{72,73} The striking effect that the heavier phase interposes between the lighter phase and the gas (see also Refs. 75 and 76) appears to have a rather simple explanation. According to our considerations in Sec. III, the more volatile phase which tends towards the vapor has the lower number density, and it happens that this goes along with a higher

mass density resulting in this surprising behavior.^{52,55}

Two wetting transitions concerning the wetting of a wall by a binary liquid mixture have been reported: glass/methanol-cyclohexane⁷¹ and silica/water-(2,6-lutidine).^{33,77} In the latter example the transition was found to be first-order and the corresponding prewetting line was identified. This corresponds to a part of S_3 in Fig. 3(a) with the only difference that the water-(2,6-lutidine) mixture has a lower critical end point.

It seems, then, that in the system we have addressed there have been very few determinations of the order of wetting transitions and much experimental work remains. One aim of this paper has been to provide some guidance for this work.

ACKNOWLEDGMENTS

One of us (M.S.) would like to thank the Institut for Teoretisk Fysikk, Universitetet i Trondheim, for their hospitality while this work was written. It was supported in part by the National Science Foundation under Grant No. DMR-83-19301.

APPENDIX

In this appendix we show that the separatrix for the order of interfacial wetting in a binary liquid mixture and the transition temperature for critical wetting as calculated numerically by Tarazona *et al.*⁴ do agree with our analytic sharp-kink expressions in Sec. III. Tarazona *et al.* consider a binary liquid mixture in which atoms of type i interact with those of types j with a long-range van der Waals potential of the form

$$\tilde{w}_{ij}(r) = \begin{cases} 0, & r < \sigma \\ -\epsilon_{ij}/(r/\sigma + \nu_{ij})^6, & r > \sigma \end{cases} \quad (\text{A1})$$

With these particle-particle potentials the coefficients $t_{3,ij}$ and $t_{4,ij}$ of Eq. (3.16) are

$$t_{3,ij} = \pi \epsilon_{ij} \sigma^6 / 6 \quad (\text{A2})$$

and

$$t_{4,ij} = -3\pi \nu_{ij} \epsilon_{ij} \sigma^7 / 5 \quad (\text{A3})$$

In Ref. 4 the value of ϵ_{ij} and ν_{ij} are not given directly, however. Rather, Tarazona *et al.* define the total strengths

$$a_{ij} = - \int d^3r \tilde{w}_{ij}(r), \quad (\text{A4})$$

and the second moments of the potentials

$$f_{ij} = - \int d^3r r^2 \tilde{w}_{ij}(r), \quad (\text{A5})$$

from which they form the dimensionless ratio

$$\eta_{ij} = f_{ij} / (a_{ij} \sigma^2). \quad (\text{A6})$$

For the special case $\nu_{ij} = 0$, this ratio takes the value $\eta_{ij} = 3$. In the vicinity of this special value, which will turn out to be the most interesting parameter region, we can express ϵ_{ij} and ν_{ij} in terms of a_{ij} and η_{ij} and thereby obtain $t_{3,ij}$ and $t_{4,ij}$ which we need. From Eqs. (A1) and (A4)–(A6) we have

$$a_{ij} = (2\pi/15)\sigma^3\epsilon_{ij}(1+v_{ij})^{-5}(v_{ij}^2+5v_{ij}+10) \quad (\text{A7})$$

and

$$\eta_{ij} = 6(v_{ij}^4 + 5v_{ij}^3 + 10v_{ij}^2 + 10v_{ij} + 5)/(v_{ij}^2 + 5v_{ij} + 10). \quad (\text{A8})$$

From Eqs. (A7) and (A8) we get

$$t_{3,ij} = (\sigma^3 a_{ij}/8)[1 + (\eta_{ij} - 3) + O((\eta_{ij} - 3)^2)] \quad (\text{A9})$$

and

$$t_{4,ij} = -(4\sigma/5)(\eta_{ij} - 3)t_{3,ij} + O((\eta_{ij} - 3)^2). \quad (\text{A10})$$

Tarazona *et al.* further restrict their potentials to

$$a_{22}/a_1 = 1.21, \quad (\text{A11a})$$

$$a_{12}/a_{11} = 0.88, \quad (\text{A11b})$$

and

$$v_{11} = v_{22} = 0. \quad (\text{A11c})$$

We can now evaluate the coefficients a_J, a_K, a_C and b_J, b_K, b_C of Eqs. (3.19) and (3.20). We find in the vicinity of $\eta_{12} = 3$

$$a_J/a_0 = 1 - 3.911(\eta_{12} - 3), \quad (\text{A12a})$$

$$a_K/a_0 = 8.822[1 + 0.443(\eta_{12} - 3)], \quad (\text{A12b})$$

$$a_C/a_0 = -0.467 \quad (\text{A12c})$$

where

$$a_0 = 0.0070\sigma^3 a_{11} \quad (\text{A12d})$$

and

$$b_J/(\sigma a_0) = 2.086(\eta_{12} - 3), \quad (\text{A13a})$$

$$b_K = -b_J, \quad (\text{A13b})$$

$$b_C = 0. \quad (\text{A13c})$$

We can determine from Eq. (3.18) the coefficients a and b in the expansion of the surface free energy, Eq. (3.17). Let us first focus on b . From (A11) and (3.18) we get

$$b = -b_J[(Q_\alpha - Q_\beta)(Q_\beta - Q_\gamma) - (M_\alpha - M_\beta)(M_\beta - M_\gamma)]. \quad (\text{A14})$$

Note that Tarazona *et al.* denote the vapor as the α phase, whereas we call it γ . They call the bulk liquid γ ; we call it α . The intruding film is formed in both cases by the β phase. Contrary to our notation in the main text, in the

numerical calculation of Ref. 4, which we want to analyze, the bulk liquid is B rich and the wetting film is A rich ($A \equiv 1, B \equiv 2$). Furthermore, the overall density of the bulk liquid is higher than the overall density of the phase which wets the liquid-vapor interface. Translated in the language of Eq. (A14) we have $M_\alpha < 0, M_\beta > 0, M_\gamma \equiv 0, Q_\alpha > Q_\beta, Q_\beta > 0$, and $Q_\gamma \equiv 0$. This means that the square bracket in Eq. (A14) is positive along the whole triple line, and therefore especially at the wetting temperature T_W . Combining Eqs. (A13a) and (A14), our sharp-kink expressions for the separatrix applied to the numerical analysis of Tarazona predicts for their model

$$\eta_{12} \gtrless 3 \leftrightarrow \left\{ \begin{array}{l} \text{first-} \\ \text{second-} \end{array} \right\} \text{ order wetting}. \quad (\text{A15})$$

Equation (A15) coincides with the numerical data presented in Fig. 10 of Ref. 4.

Next we construct the coefficient $a(T)$ from Eqs. (3.18) and (A12). Because in the model of Tarazona *et al.* all hard-core radii are equal to σ , the low temperature densities of the A -rich and B -rich liquid phases are equal. Therefore, the condition of Eq. (3.24) gives together with Eq. (A9) the necessary condition $\eta_{12} < 3.375$ for critical wetting. Going beyond the linear approximation in Eq. (A9) one finds that for $\eta_{12} < 3.13$ ($\eta_{12} > 3.13$) $l = \infty$ is a local maximum (minimum) of $\Omega_s(l, T=0)$. This condition is indeed satisfied in the region $\eta_{12} < 3$ for which Tarazona *et al.* find critical wetting. On the other hand, the fact that they find a first-order wetting transition in the region $\eta_{12} > 3.13$ is no surprise because in that region $\Omega_s(l, T=0)$ has already a local minimum at $l = \infty$. Only in the narrow regime $3 < \eta_{12} < 3.13$ the wetting transition is driven to first-order by the next-to-leading-order term in the expansion of Ω_s . Finally, we have to check whether $a(T)$ can change sign from a negative to a positive value at $T_W < T_{cep}$. For that purpose one needs explicitly the temperature dependence of the six bulk densities $M_{\alpha,\beta,\gamma}, Q_{\alpha,\beta,\gamma}$ along the triple line. Fortunately, sufficient data about them can be read off from Figs. 1–3 and 7 in Ref. 4 and from Fig. 2 in Ref. 52 to decide this question.⁷⁸ In doing so we confirmed two features of the sharp-kink approximation: (1) In the case of critical wetting the numerical values of T_W which Tarazona *et al.* report coincide with the temperatures at which a vanishes. (2) In the case of first-order wetting the transition temperatures as calculated from the full MFE's are higher than the corresponding temperatures at which a change sign. This reflects the contribution of the smooth kink to the higher-order terms in the expansion of $\Omega_s(l)$ which are important for T_W of a first-order wetting transition.

¹R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B **26**, 5112 (1982).

²H. Nakanishi and M. Fisher, Phys. Rev. Lett. **49**, 1565 (1982).

³P. Tarazona and R. Evans, Mol. Phys. **48**, 799 (1983).

⁴P. Tarazona, M. M. Telo de Gama, and R. Evans, Mol. Phys. **49**, 283 (1983).

⁵R. Evans and P. Tarazona, J. Chem. Phys. **80**, 587 (1983).

⁶R. E. Benner, Jr., G. F. Teletzke, L. E. Scriven, and H. T. Davis, J. Chem. Phys. **80**, 589 (1983).

⁷M. E. Costas, C. Varea, and A. Robledo, Phys. Rev. Lett. **51**, 2394 (1983).

⁸M. P. Nightingale, W. F. Saam, and M. Schick, Phys. Rev. Lett. **51**, 1275 (1983).

⁹P.-G. de Gennes, C. R. Acad. Sci. Ser. B **297** 9 (1983).

- ¹⁰V. Privman, *J. Chem. Phys.* **81**, 2463 (1984).
- ¹¹M. P. Nightingale, W. F. Saam, and M. Schick, *Phys. Rev. B* **30**, 3830 (1984).
- ¹²R. Lipowsky, *Z. Phys. B* **55**, 345 (1984).
- ¹³R. Lipowsky and D. M. Kroll, *Phys. Rev. Lett.* **52**, 2303 (1984).
- ¹⁴D. M. Kroll and T. F. Meister, *Phys. Rev. B* **31**, 392 (1985).
- ¹⁵S. Dietrich and M. Schick, *Phys. Rev. B* **31**, 4718 (1985).
- ¹⁶C. Ebner, W. F. Saam, and A. K. Sen, *Phys. Rev. B* **31**, 6134 (1985); **32**, 1558 (1985).
- ¹⁷T. Aukrust and E. H. Hauge, *Phys. Rev. Lett.* **54**, 1814 (1985).
- ¹⁸D. M. Kroll, R. Lipowsky, and R. K. P. Zia, *Phys. Rev. B* **32**, 1862 (1985).
- ¹⁹S. Dietrich, M. P. Nightingale, and M. Schick, *Phys. Rev. B* **32**, 3182 (1985).
- ²⁰I. K. Snook and D. Henderson, *J. Chem. Phys.* **68**, 2134 (1978).
- ²¹I. K. Snook and W. van Meegen, *J. Chem. Phys.* **70**, 3099 (1979).
- ²²J. E. Laue, T. H. Spurling, B. C. Freasier, J. W. Perram, and E. R. Smith, *Phys. Rev. A* **20**, 2147 (1979).
- ²³D. E. Sullivan, D. Levesque, and J. J. Weis, *J. Chem. Phys.* **72**, 1170 (1980).
- ²⁴C. Ebner, *Phys. Rev. A* **23**, 1925 (1981).
- ²⁵I. M. Kim and D. P. Landau, *Surf. Sci.* **110**, 415 (1981).
- ²⁶W. Selke and J. Yeomans, *J. Phys. A* **16**, 2789 (1983).
- ²⁷W. Selke, D. A. Huse, and D. M. Kroll, *J. Phys. A* **17**, 3019 (1984).
- ²⁸F. van Swol and J. R. Henderson, *Phys. Rev. Lett.* **53**, 1376 (1984).
- ²⁹I. Sega, W. Selke, and K. Binder, *Surf. Sci.* **154**, 331 (1985).
- ³⁰(a) K. Binder and D. P. Landau, *J. Appl. Phys.* **57**, 3306 (1985). (b) K. Binder, D. P. Landau, and D. M. Kroll, *J. Magn. Magn. Mater.* (to be published).
- ³¹D. J. Lee, M. M. Telo da Gama, and K. E. Gubbins, *Mol. Phys.* **53**, 1113 (1984).
- ³²D. J. Lee, M. M. Telo da Gama, and K. E. Gubbins, *J. Phys. Chem.* **89**, 1514 (1985).
- ³³D. Beysens and D. Estève, *Phys. Rev. Lett.* **54**, 2123 (1985).
- ³⁴M. M. Telo de Gama and R. Evans, *Mol. Phys.* **48**, 687 (1983).
- ³⁵I. Hadjiagapiou and R. Evans, *Mol. Phys.* **54**, 383 (1985).
- ³⁶B. C. Freasier and S. Nordholm, *Mol. Phys.* **54**, 33 (1985).
- ³⁷T. F. Meister and D. M. Kroll, *Phys. Rev. A* **31**, 4055 (1985).
- ³⁸W. E. Carlos and M. W. Cole, *Surf. Sci.* **91**, 339 (1980).
- ³⁹The case of drying can be treated quite similarly.
- ⁴⁰Strong negative values of even higher-order terms can still bring about a first-order transition.
- ⁴¹The numerical solution of the full MFE's in Ref. 15 showed indeed that the interface is located between two lattice planes and not at a lattice plane. This justifies the lattice version of the sharp-kink approximation as described in the text.
- ⁴²In the preprint version of Ref. 16 it is stated that a repulsive substrate potential in the first layer mimics the excluded volume effect. This is sufficient but not necessary to have $d_w > 0$.
- ⁴³Similar arguments can be found in Ref. 14.
- ⁴⁴D. A. Huse, *Phys. Rev. B* **29**, 6985 (1984).
- ⁴⁵F. T. Gittes and M. Schick, *Phys. Rev. B* **30**, 209 (1984).
- ⁴⁶C. Ebner, *Phys. Rev. B* **28**, 2890 (1983).
- ⁴⁷R. Pandit and M. Fisher, *Phys. Rev. Lett.* **51**, 1772 (1983).
- ⁴⁸M. Blume, V. Emery, and R. B. Griffiths, *Phys. Rev. A* **4**, 1071 (1971).
- ⁴⁹D. Mukamel and M. Blume, *Phys. Rev. A* **10**, 610 (1974).
- ⁵⁰P. H. van Konynenburg and R. L. Scott, *Philos. Trans. R. Soc. Lond. Ser. A* **298**, 495 (1980).
- ⁵¹D. Furman, S. Dattagupta, and R. B. Griffiths, *Phys. Rev. B* **15**, 441 (1977).
- ⁵²P. Tarazona, M. M. Telo da Gama, and R. Evans, *Mol. Phys.* **49**, 301 (1983).
- ⁵³M. M. Telo da Gama and R. Evans, *Mol. Phys.* **48**, 229 (1983).
- ⁵⁴S. Dietrich (unpublished).
- ⁵⁵R. Lipowsky, *Phys. Rev. B* **32**, 1731 (1985).
- ⁵⁶At first glance Tarazona *et al.* (Ref. 4) studied only a one-dimensional subspace of \mathcal{P} . However, the value of \bar{w}_{11} , which they fixed, gives only the temperature scale so that their results correspond effectively to a two-dimensional subspace of \mathcal{P} .
- ⁵⁷E. H. Hauge and M. Schick, *Phys. Rev. B* **27**, 4288 (1983).
- ⁵⁸Yu. S. Barash and V. L. Ginzburg, *Usp. Fiz. Nauk.* **143**, 345 (1984) [*Sov. Phys. Usp.* **27**, 467 (1984)].
- ⁵⁹E. S. Sabsky and C. H. Anderson, *Phys. Rev. A* **7**, 790 (1973).
- ⁶⁰R. F. Kayser, J. W. Schmidt, and M. R. Moldover, *Phys. Rev. Lett.* **54**, 707 (1985).
- ⁶¹I. E. Dzyaloshinskii, E. M. Lifschitz, and L. P. Pitaevskii, *Adv. Phys.* **10**, 165 (1961).
- ⁶²M. Bienfait, *Surf. Sci.* **162**, 411 (1986).
- ⁶³J. Suzanne, J. L. Seguin, M. Bienfait, and E. Lerner, *Phys. Rev. Lett.* **52**, 637 (1984).
- ⁶⁴J. M. Gay, M. Bienfait, and J. Suzanne, *J. Phys. (Paris)* **45**, 1497 (1984).
- ⁶⁵Y. Carmi, S. G. Lipson, and E. Polturak, *Phys. Rev. Lett.* **54**, 2042 (1985).
- ⁶⁶A. D. Migone, J. Krim, J. G. Dash, and J. Suzanne, *Phys. Rev. B* **31**, 7643 (1985).
- ⁶⁷J. Krim and J. G. Dash, *Surf. Sci.* **162**, 421 (1986).
- ⁶⁸W. F. Saam (private communication).
- ⁶⁹For reference to earlier work which reports first-order wetting transitions, see D. E. Sullivan, *J. Chem. Phys.* **74**, 2604 (1981).
- ⁷⁰J. Krim, J. G. Dash, and J. Suzanne, *Phys. Rev. Lett.* **52**, 640 (1984).
- ⁷¹M. R. Moldover and J. W. Cahn, *Science* **207**, 1073 (1980).
- ⁷²J. W. Schmidt and M. R. Moldover, *J. Chem. Phys.* **79**, 379 (1983).
- ⁷³M. R. Moldover and J. W. Schmidt, *Physica* **12D**, 351 (1984).
- ⁷⁴V. Vani, S. Guha, E. S. R. Gopal, and S. Madhusudana Rao, *Phys. Lett.* **99A**, 441 (1983).
- ⁷⁵R. B. Heady and J. W. Cahn, *J. Chem. Phys.* **58**, 896 (1973).
- ⁷⁶O'D. Kwon, D. Beaglehole, W. W. Webb, B. Widom, J. W. Schmidt, J. W. Cahn, M. R. Moldover, and B. Stephenson, *Phys. Rev. Lett.* **48**, 185 (1982).
- ⁷⁷D. W. Pohl and W. I. Goldburg, *Phys. Rev. Lett.* **48**, 1111 (1982).
- ⁷⁸Note that although Ref. 52 deals only with short-range potentials the bulk densities in Fig. 2 of Ref. 52 can be used for the sharp-kink approximation because the bulk parameters a_{ij} are the same as in Ref. 4.