Continuous and first-order wetting transition from the van der Waals theory of fluids

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The transition between incomplete wetting and complete wetting of an attractive substrate in contact with a gas at gas-liquid coexistence is studied. Within the framework of the systematic van der Waals (mean-field) theory of fluids, it is shown that both a continuous wetting transition, as found by Sullivan, and a first-order transition with a prewetting line, previously found by other methods, are possible. The relative magnitude of the various characteristic lengths in the problem is shown to be of relevance in this context. Beyond the model calculations, purely thermodynamic arguments show that in general the prewetting line, if it exists, joins the bulk coexistence line tangentially in the T- μ phase plane. The manner in which the difference in slope vanishes as bulk coexistence is approached is closely related to the nature of the forces.

I. INTRODUCTION

The phenomenological characterization of an adsorbing surface in the presence of liquid-gas equilibrium is well known^{1,2}: Either the liquid completely wets the surface or it does not. In the latter case droplets of liquid appear on the surface with a finite angle of contact. The former case is obtained in the limit that the angle vanishes. In contrast to the familiarity of these results, the *transition* between these states, the way either of them is approached in systems not initially at coexistence, and the connections between microscopic interactions and macroscopic behavior, have only recently come under study.³

In the case of strongly attractive substrates, approach to coexistence leads to an adsorbed film that grows either continuously or via a series of steps, depending on the temperature.⁴ As coexistence is approached, the thickness of the film grows without bounds, producing at coexistence a completely wet surface. For weaker substrates the film thickness, and thus the excess surface density, remains finite as coexistence is reached. Thus the surface remains incompletely wet. As first noted by Cahn⁵ a surface which is incompletely wet at low temperatures is expected to become completely wet as the critical temperature of the bulk system is approached. The change from one condition to the other is denoted the wetting transition and the corresponding temperature the wetting temperature T_w . This transition is defined only at bulk coexistence.

If the wetting transition is first order, by continui-

ty we expect a line of first-order thin-film to thickfilm transitions extending into the $(T, \Delta \mu)$ plane (Tis the temperature, $\Delta \mu$ is the deviation of the chemical potential from its value at bulk coexistence), and terminating in a critical point.^{5,6} The locus of these transitions, $\Delta \mu = \Delta \mu_{pw}(T)$, is denoted the prewetting line. The location $(T_{pwc}, \Delta \mu_{pwc})$ of its critical end point must depend upon the properties of the substrate as well as on the interparticle interactions. If $|\Delta \mu_{pwc}|$ decreases with decreasing strength ϵ of the substrate potential, then there exists a critical value ϵ_{cw} of this strength such that $\Delta \mu_{pwc}=0$. At this point the wetting transition becomes continuous. As there is every reason to expect the wetting transition to persist over a finite range of even weaker sub-



FIG. 1. Topology of the phase diagram for not too low temperatures. Heavy lines correspond to continuous transitions. The dashed line at coexistence $(\Delta \mu = 0)$ and the connected sheet shaded below coexistence indicate the location of first-order transitions. The wetting transitions change from continuous to first order at substrate strength ϵ_{cw} .

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strate potentials, presumably the transition remains continuous over this range. Such a continuous transition is denoted critical wetting. The topology of the phase diagram as a function of T, $\Delta\mu$, and ϵ is shown in Fig. 1.

The phenomenological picture sketched above, which ignores possible transitions associated with successive layering, emerges from the continuum mean-field results of Pandit and co-workers.^{7,3} Earlier efforts had revealed various aspects of this picture. On the one hand, the elegant experiments by Moldover and Cahn⁸ on a related system are consistent with a first-order transition at coexistence. Furthermore, prewetting, but not critical wetting, had been observed in calculations based on the square-gradient approximation^{5,6} and in mean-field⁹ and Monte Carlo¹⁰ calculations for particular potentials and parameter values. On the other hand, Sullivan in two important papers,¹¹ had convincingly demonstrated critical wetting and complete absence of prewetting, in a systematic mean-field approach to a particular class of substrate and interparticle forces. The qualitative difference between the Pandit-Wortis and the Sullivan pictures could be attributed both to the difference in the interactions used and to the nature of the mean-field theory employed. Sullivan's calculations are within the systematics of the modern van der Waals theory¹² (see Sec. III), whereas it is not easy to fit the calculations of Pandit and Wortis into this framework.

The main purpose of this paper is to show that the difference in methodology between Sullivan and Pandit-Wortis is *not* responsible for the qualitative difference in results. By two perturbation calculations around Sullivan's model, we get results that lend support to the Pandit-Wortis picture of Fig. 1. In addition, however, the results indicate that the relative range of the forces can be relevant to the nature of the wetting transition.

Before entering into the model calculations, we show in Sec. II that one can derive some interesting information about the prewetting line (if it exists) from thermodynamics alone. In Sec. III the van der Waals background is sketched and the Sullivan model, basic to the perturbation calculations that follow, is presented in some detail. In Sullivan's model both the substrate and the integrated interparticle potential are exponential with precisely the same range. Section IV contains the firstperturbation expansion, in which the range of the substrate potential is made slightly longer than that of the interparticle potential. Within this perturbation scheme Sullivan's conclusions remain valid, nothing but critical wetting is observed. The range of validity of this scheme is found to be restricted, however, leaving open the possibility of prewetting

beyond this range. The results of Sec. IV suggest the second-perturbation scheme, explored in Sec. V, in which a weak long-range tail is added to the substrate potential. In this case prewetting is indeed found. Concluding remarks are made in Sec. VI.

II. THERMODYNAMICS OF THE PREWETTING LINE

In this section we shall call attention to a Clapeyron-type equation for lines of first-order transitions, both between bulk phases and surface phases, in the (T,μ) plane. With additional assumptions on the growth of the wetting layer as bulk coexistence is approached, this equation is sufficiently powerful to allow definite predictions on the manner in which the prewetting line (if it exists) connects to the bulk coexistence line.

For an open system, with given volume V, the exchange of particles and energy with the surroundings is governed by the chemical potential μ and the temperature T. The differential of the appropriate thermodynamic potential Ω is¹

$$d\Omega = -S \, dT - N \, d\mu \,, \qquad (2.1)$$

where N and S denote the total number of particles and the total entropy in V. When surface effects are disregarded, $\Omega = -pV$ and $d\Omega = -Vdp$, where p is the pressure. Since thermodynamic stability requires Ω to be minimal, two phases (1 and 2) can only coexist if $\Omega_1 = \Omega_2$. Along a line in the (T,μ) plane, corresponding to coexistence between the bulk phases, one must therefore have $d\Omega_1 = d\Omega_2$, i.e.,

$$\left|\frac{d\mu}{dT}\right|_{b} = -\frac{S_2 - S_1}{N_2 - N_1} , \qquad (2.2)$$

where subscript b stands for bulk.

The thermodynamics of surface effects can be extracted from (2.1) by subtraction of the bulk part which dominates all extensive quantities. The bulk parts are defined on the basis of the associated densities at given μ , T so that

$$N_{b} = \rho(\mu, T)V, \quad N_{s} = N - N_{b} ,$$

$$S_{b} = \sigma(\mu, T)V, \quad S_{s} = S - S_{b} ,$$

$$\Omega_{b} = -p(\mu, T)V, \quad \Omega_{s} = \Omega + pV .$$
(2.3)

Here subscript *s* denotes the excess surface contribution to the corresponding quantities.

The Clapeyron-type equation for first-order coexistence lines between two surface phases follows immediately from (2.1) and (2.3) as

$$\left[\frac{d\mu}{dT}\right]_{s} = -\frac{S_{s2} - S_{s1}}{N_{s2} - N_{s1}}, \qquad (2.4)$$

in complete analogy with (2.2).

A note of caution on the application of (2.2) and (2.4) is in order. In phenomenological thermodynamics the chemical potential is only defined up to a linear function of T. This reflects the arbitrariness of the zero point of S and of μ . Consequently, $d\mu/dT$ is, in thermodynamics, defined only up to an additive constant.¹³ Furthermore, in theoretical discussions of phase equilibria based on classical statistical mechanics, the kinetic degrees of freedom play no part, since they give contributions to the entropy per particle, and to μ , which are independent of the phase and are determined by the temperature alone. Only configurational contributions to S and μ need therefore be considered. As a result, the coexistence lines in the (T,μ) plane are distorted, and the quantities in (2.2) and (2.4) must be reinterpreted accordingly.

Generally, the competing surface phases are both thin, with a thickness of a few molecular layers. The special feature of the prewetting line (if it exists) is that one of the competing phases is a liquidlike layer with a thickness that tends to infinity as bulk coexistence is approached from the gas side. Capitalizing on the special properties of this thick film, one can extract more information from (2.4).

Consider a fluid at (or slightly below) gas-liquid (bulk) coexistence, in contact with an attractive substrate. Assume the temperature to be at or above the wetting temperature T_w . Disregarding transverse variation, one can describe the fluid near the substrate by the density profile $\rho(x)$, where x > 0 is the distance from the substrate (Fig. 2). Let this thick phase be 2. The excess number of particles with respect to the bulk gas can be written

$$N_{s2} = A[n_{sw2} + (\rho_l - \rho_g)l + n_{si}].$$

Here A is the transverse area, n_{sw2} and n_{si} are the



FIG. 2. Typical density profile of a thick film wetting the substrate, which is located at x = 0. The shaded regions with areas n_{sw2} and n_{si} represent excess surface densities of the two transition layers. The thickness of the liquid layer is l.

excess surface densities associated with the transition layer at the wall and the interface, respectively, ρ_l and ρ_g are the liquid and gas (volume) densities, and l is the thickness of the liquid layer. In analogous notation one can write the excess surface entropy as

$$S_{s2} = A[s_{sw2} + (\sigma_l - \sigma_g)l + s_{si}]$$

The thin phase (phase 1) amounts to nothing more than a transition layer close to the wall, so

$$N_{s1} = An_{sw1}, S_{s1} = A\sigma_{sw1}$$

Insertion of these expressions into (2.4) yields for the prewetting line

$$\left[\frac{d\mu}{dT}\right]_{pw} = -\frac{s_{sw2} + s_{si} - s_{sw1} + (\sigma_l - \sigma_g)l}{n_{sw2} + n_{si} - n_{sw1} + (\rho_l - \rho_g)l} \quad .$$
(2.5)

As coexistence is approached, $l \rightarrow \infty$, so that

$$\left[\frac{d\mu}{dT}\right]_{\rm pw} \rightarrow -\frac{\sigma_l - \sigma_g}{\rho_l - \rho_g} = \left[\frac{d\mu}{dT}\right]_{gl}.$$
 (2.6)

Thus the prewetting line meets the coexistence line for bulk liquid and gas tangentially¹⁴ (Fig. 3).

One can go one step further. Under the assumption that all quantities in (2.5), except *l*, vary slowly as the bulk coexistence line is approached from below, one has, asymptotically,

$$\left[\frac{d\mu}{dT}\right]_{\rm pw} - \left[\frac{d\mu}{dT}\right]_{gl} \simeq -\frac{C}{l} , \qquad (2.7)$$

where C = C(T) is necessarily positive.

The dependence of l on the distance $-\Delta\mu$ from



FIG. 3. Schematic plot of surface phase boundaries in the $T, \Delta \mu$ plane, where $\Delta \mu$ is the chemical potential measured from its coexistence value. The prewetting line joins the coexistence line tangentially.

bulk coexistence has been discussed in the literature.^{3,15} For Lennard-Jones-type forces (substratefluid 9-3 and fluid-fluid 12-6) such that the long tail of the substrate-fluid force dominates, one expects $l\simeq B(T)(-\Delta\mu)^{-1/3}$. For finite-range forces (nearest neighbor or exponential), the expected behavior is $l\simeq -D(T)\ln(-\Delta\mu)$. Thus in every case the prewetting line will connect tangentially to the bulk coexistence line. However, the way in which the slope of the coexistence line is approached, reflects the nature of the microscopic interactions.

Note that the above discussion makes no reference to the value of $(d\mu/dT)_{gl}$. The absolute values of the slopes have the ambiguities mentioned earlier. Their difference does not.

Finally, if the fluid is represented by the latticegas model (the nature of the lattice being irrelevant), the configurational entropies per unit volume are the same in the liquid and gas phases.¹⁶ Consequently $(d\mu/dT)_{gl}=0$, and the results above show that in the (T,μ) plane, the prewetting line will approach the coexistence line horizontally.

III. THE SULLIVAN MODEL

A. Basics

In this section we review Sullivan's work¹¹ on a mean-field model for the wetting transition. Since Sullivan's model constitutes the starting point for the perturbation calculations of the two subsequent sections, it is necessary to present it in some detail.

Sullivan's starting point, and ours, is the van der Waals, or mean-field, theory of fluids. In its modern formulation¹² it is viewed as the lowestorder theory in which the properties of a reference system with short-range repulsive interactions are taken as known, and the effects of longer-range attractive forces are treated as perturbations. This approach to the theory of fluids has been thoroughly explored for the last 20 years. The results of these efforts indicate that, as long as one stays away from critical regions, the modern van der Waals theory (possibly including leading correction terms) gives a good account of a wide range of phenomena.

The type of interparticle potential used in the van der Waals theory is the following¹⁷:

$$\widetilde{\Phi}(r) = \begin{cases} \infty, \ r < d \\ \kappa^D v(\kappa r), \ r > d \end{cases}.$$
(3.1)

Here d is the diameter of the hard-core repulsion, D is the dimensionality, and v(r) < 0 is the attractive potential, the inverse range of which is measured by κ . The potential is parametrized in such a way that

$$\int d^{D}r \,\kappa^{D} v(\kappa r) = -\alpha \tag{3.2}$$

is independent of κ . In the van der Waals theory the quantities of interest are studied as power-series expansions in κd [or $(\kappa d)^{D}$]. The two results for uniform systems of immediate interest to us are

$$p(\rho,T) = p_h(\rho,T) - \frac{\alpha}{2}\rho^2 + O((\kappa d)^D) ,$$

$$\mu(\rho,T) = \mu_h(\rho,T) - \alpha\rho + O((\kappa d)^D) .$$
(3.3)

The pressure p_h and chemical potential μ_h of the hard-core system are assumed to be known functions of ρ and T.

When the theory is generalized to systems nonuniform¹⁸ in one direction (in our case the distance x from a solid surface), the x-dependent density is split into components with different characteristic spatial scales of variation. The longest spatial scale set by the interactions is κ^{-1} . The corresponding component $\rho(x)$ of the density obeys, to zeroth order in κd , the equation

$$\mu = \mu_{h}[\rho(x)] + \Phi(x) + \int_{0}^{\infty} dx' \chi(|x - x'|)\rho(x') . \qquad (3.4)$$

Here the function $\chi(|x-x'|)$ is the attractive interparticle interaction v(r) integrated over lateral dimensions, and the substrate potential $\Phi(x)$ is assumed to vary on the same scale as $\chi(|x|)$. For notational simplicity the scaling factor κ has been absorbed into x, and the temperature dependence of the various quantities has been suppressed.

Equation (3.4) is the basis for Sullivan's work¹¹ and for ours. It applies to situations where lateral variations can be ignored and is the lowest-order (in κd) equation for the slowly varying part $\rho(x)$ of the density. Close to the wall, where the density abruptly falls to zero, the density develops oscillations on the spatial scale of d. This part of the density is ignored in (3.4). By the same token, layering transitions are not accounted for by (3.4). In the limit $\kappa d \rightarrow 0$, (3.4) becomes exact for the slow component $\rho(x)$. However, even for realistic forces, where $\kappa d \sim 0.3$, (3.4) is expected to give a good account of the slowly varying density component $\rho(x)$, except for properties associated with criticality.

With the nonlinearity inherent in $\mu_h(\rho)$, the integral equation (3.4) resists easy analytical progress. Following Sullivan, however, we now adopt the simplifying *first assumption*: The interparticle attraction is of the *D*-dimensional Yukawa form, i.e., after lateral integration,

$$\chi(|x|) = -\frac{\alpha}{2}e^{-|x|} . \qquad (3.5)$$

This choice is not based on physical considerations, but is made for mathematical convenience. Differentiating (3.4) twice with respect to x and eliminating the integral by (3.4), one finds

$$\frac{d^{2}\mu_{h}}{dx^{2}} = \mu_{h}[\rho(x)] - \mu - \alpha\rho(x) + \Phi(x) - \Phi''(x) .$$
(3.6)

Knowing the monotonic function $\mu_h(\rho)$, one can invert to find $\rho = \rho(\mu_h)$. Thus the integral equation (3.4) for this special choice of $\chi(|x|)$ has been turned into a second-order nonlinear differential equation for μ_h , with inhomogeneous terms due to the substrate potential $\Phi(x)$.

Sullivan proceeds by making a second assumption:

$$\Phi(x) = -\epsilon e^{-x} , \qquad (3.7)$$

i.e., $\Phi(x)$ is also exponential with precisely the same range as $\chi(|x|)$. With this assumption, the inhomogeneous terms in (3.6) cancel to give

$$\frac{d^2\mu_h}{dx^2} = \mu_h[\rho(x)] - \mu - \alpha\rho(x) . \qquad (3.8)$$

The differential equations (3.6) or (3.8) must be supplemented by two boundary conditions. As the boundary condition at infinity, we shall always insist that the bulk fluid is a gas, $\rho(x \to \infty) = \rho_g$. The boundary condition on the wall (i.e., at x = 0) for exponential interactions (3.5) follows from the same type of argument as that leading to (3.6):

$$\left(\frac{d\mu_h}{dx}\right)_{x=0} = \mu_h[\rho(0)] - \mu + \Phi(0) - \Phi'(0) , \qquad (3.9)$$

or, with Sullivan's second assumption (3.7)

$$\left.\frac{d\mu_h}{dx}\right|_{x=0} = \mu_h[\rho(0)] - \mu - 2\epsilon . \qquad (3.10)$$

In Sullivan's case the substrate potential $\Phi(x)$ does not affect the differential equation (3.8). It does, however, enter through the boundary condition (3.10). For any form of $\Phi(x)$ other than (3.7), the substrate potential will influence *both* the differential equation (3.6) and the boundary condition (3.8). In this paper we adhere to Sullivan's first assumption (3.5) in order to trade the complexities of the integral equation (3.4) for the relative simplicity of the differential equation (3.6) with (3.9). In Secs. III B and III C we shall, however, cautiously move away from Sullivan's second assumption (3.7).

B. The dynamical analog

Before moving away from Sullivan's second assumption, we shall reformulate the problem as one in classical mechanics.¹⁸ For concreteness we shall also invoke the simplest possible model for $p_h(\rho)$ and $\mu_h(\rho)$, namely the lattice-gas model. The results do not in any essential way depend on this choice. For the lattice gas one has

$$p_{h}(\rho) = -k_{B}T\ln(1-\rho) ,$$

$$\mu_{h}(\rho) = k_{B}T\ln\frac{\rho}{1-\rho} , \qquad (3.11)$$

$$\rho(\mu_{h}) = \left[\exp\left(-\frac{\mu_{h}}{k_{B}T}\right] + 1\right]^{-1} ,$$

where k_B is Boltzmann's constant. Note that $\mu_h(\rho)$ is the *configurational* chemical potential of the lattice gas. With this choice for $\mu_h(\rho)$, a standard calculation based on (3.3) shows that the chemical potential μ at gas-liquid coexistence has the value

$$\mu_{gl} = -\frac{\alpha}{2} \ . \tag{3.12}$$

The dynamical language is introduced when we let $x \rightarrow t$ and treat t as a time variable. Furthermore, we use the dimensionless variables

$$\frac{\mu_h}{k_B T} = \xi, \quad \frac{1}{k_B T} \frac{d\mu_h}{dx} = \dot{\xi} , \qquad (3.13)$$

$$\frac{\alpha}{k_BT} = A, \ \frac{\epsilon}{k_BT} = E, \ \frac{\mu - \mu_{gl}}{k_BT} = \frac{\mu - 2}{k_BT} = M$$

(where ξ plays the role of a "position" and ξ plays the role of a "velocity"). In these variables (3.8) reads

$$\ddot{\xi} = \xi - M + \frac{A}{2} - \frac{A}{e^{-\xi} + 1} = -\left[-\xi + M + \frac{A}{2} \tanh \frac{\xi}{2}\right] = -\frac{dV}{d\xi} .$$
 (3.14)

Thus Sullivan's model is equivalent to the problem of a classical particle of mass unity, moving in the one-dimensional potential $V(\xi)$. The arbitrary constant in V is conveniently chosen such that at a ξ corresponding to the gas density, V vanishes, i.e., $V(\xi(\rho_g))=0$. Energy conservation gives

$$\frac{1}{2}\dot{\xi}^2 + V(\xi) = W$$
, (3.15)

where W is the total energy. Solving for $\dot{\xi}$ one has

$$\xi = \pm \{2[W - V(\xi)]\}^{1/2}$$
. (3.16)

The boundary condition on the wall for Sullivan's case, (3.10), is translated into the initial condition

$$\dot{\xi}(0) = \xi(0) - M + \frac{A}{2} - 2E$$
 (3.17)



FIG. 4. Potential energy $V(\xi)$ sketched as a function of "position" ξ (a) below coexistence, M < 0, and (b) at coexistence, M = 0.

Figure 4 shows a qualitative plot of $V(\xi)$, (a) below (i.e., on the gas side of) coexistence, M < 0, and (b) at coexistence, M = 0. Figure 5 shows corresponding plots of the trajectories of the continuous map generated by (3.16) at various energies W. The heavy curve corresponds to W=0. The boundary condition $\rho(x \to \infty) = \rho_g$ clearly translates into the requirement that the particle should end up on the "gas peak" in Fig. 4, with zero energy, i.e., only the heavy trajectories of Fig. 5 are allowed. The initial condition (3.17) is plotted as dashed lines of slope unity in Fig. 5. The different positions of the dashed lines 1, 2, and 3 in Fig. 5(b) reflect increasing values of E, the (dimensionless) amplitude of the substrate attraction.

The solution $\xi(t)$ for the case M < 0, Fig. 5(a), is clearly unique: At t=0 the particle starts at the intersection of the lower heavy W=0 trajectory and the dashed line, and moves to the left until it asymptotically ends up at $\xi = \xi_g$, $\dot{\xi} = 0$. At coexistence, M=0, again only the lower branch of the W=0trajectory is, by continuity, of relevance. This time, however, the nature of the solution, $\xi(t)$, depends crucially upon the position of the dashed line. The marginal case is represented by line 2, corresponding to substrate strength $E = E_0$ (or $\epsilon = \epsilon_0$) for which

$$\dot{\xi}(0) = \phi + \frac{A}{2} - 2E_0 = 0$$
. (3.18)

Here we have defined ϕ as $\phi = \xi(\rho = \rho_l, M = 0)$, which is determined from (3.14) by $(dV/d\xi)_{\xi=0}=0$, i.e.,

$$\phi = \frac{A}{2} \tanh \frac{\phi}{2} . \qquad (3.19)$$

Use of (3.11) and (3.13) in (3.18) gives¹⁹

$$E_0 = \frac{A}{2} \rho_l(T)$$

or

$$\epsilon_0 = \frac{\alpha}{2} \rho_l(T) \; .$$

With (3.18)-(3.20) the initial condition (3.17) can be written

$$\xi(0) = \xi(0) + 2(E_0 - E) - \phi - M$$
. (3.21)

When $E < E_0$ [line 1 in Fig. 5(b)], the particle rapidly finds its way to the gas peak, corresponding to the substrate being incompletely wet. When, on the other hand, $E > E_0$ (line 3) the particle slows down on approaching the liquid hill and (as $M \rightarrow 0^-$) takes a (logarithmically) infinite time to pass it. This corresponds to a liquid film completely wetting the substrate. As the temperature increases $\rho_I(T)$, and thus ϵ_0 , decreases and the thickness of the liquid film grows continuously as the dashed line moves to the



FIG. 5. The dynamical trajectories (solid lines) in the (ξ, ξ) phase plane (a) below coexistence, M < 0, and (b) at coexistence, M=0, for various total energies W. The heavily drawn trajectories correspond to W=0. The dashed lines represent initial conditions for various substrate attractions.

(3.20)

C. The free energy

We shall also need the expression for the free energy. For any van der Waals model governed by (3.4), the excess surface free energy per unit substrate area, $\gamma_{sg} = \Omega_s / A$, is given by Eq. (A1) of the Appendix.

Sullivan has shown¹¹ that in the special case considered by him the (dimensionless) free energy can be given a geometric interpretation in terms of the $\xi - \xi$ diagrams of Fig. 5. As pictured in Fig. 6, γ_{sg} is (apart from a constant term) given as the area between the dynamical trajectory, the initial condition line, and the ξ axis. Unfortunately, this appealing picture does not carry over to the more general case. We shall nevertheless have occasion to use it as it does apply in a special situation considered in Sec. V.

IV. THE FIRST-PERTURBATION SCHEME

We now relax Sullivan's second assumption and let the substrate potential have the form

$$\Phi(x) = -\epsilon e^{-\beta x} , \qquad (4.1)$$

where the inverse dimensionless range β of the substrate potential is assumed to be close to unity. In the dynamical language of (3.13) the differential equation (3.14) for μ_h now takes the form

$$\ddot{\xi} = -\frac{dV}{d\xi} + F(t) \tag{4.2}$$

with

$$F(t) = -E(1-\beta^2)e^{-\beta t}$$

The potential $V(\xi)$ is the same as in (3.14), but, in addition, there is now a transient external force F(t). We shall mostly be interested in the case where the range of the substrate potential is longer than that of the interparticle forces. In that case $\beta < 1$, and F(t)pushes the "particle" to the left in Figs. 4 and 5.

At coexistence, Fig. 5(b), the question of whether



FIG. 6. Surface free energy in Sullivan's case. To $-E^2$ should be added the value of the shaded area in the the (ξ, ξ) plane.

the substrate is completely or incompletely wet is, in the dynamical picture, decided by what happens close to the liquid peak, i.e., close to $\xi = \phi$. By continuity, the thickness of the film close to coexistence is also determined there. If β is close to 1, F(t) is small. The external force will therefore have a negligible effect on the trajectory of the particle unless the initial condition line crosses the ξ axis in Fig. 5 close to $\xi = \phi$. Thus the perturbing force can only be of qualitative relevance if E is close to E_0 , given by (3.20). Also, if M is sizable (and negative), F(t) becomes largely irrelevant. We shall consequently consider $1-\beta$, F(t), $E-E_0$ (or $\epsilon - \epsilon_0$), and M (or $\mu - \mu_{gl}$) as small quantities. It will later become apparent that with $1-\beta$ and $E-E_0$ considered as of first order, M must be taken as small of second order. With

$$\xi = \phi + \xi_1 + \xi_2 + \cdots$$
, (4.3)

where ξ_n is considered small of *n*th order, linearization of (4.2) gives

$$\ddot{\xi}_1 - \lambda^2 \xi_1 = -E(1 - \beta^2) e^{-\beta t}$$
, (4.4)

where [with use of (3.8), (3.13), (3.3), and $(\partial p / \partial \mu)_T = \rho$],

$$\lambda^{2} = -\frac{d^{2}V}{d\xi^{2}} = \frac{\partial}{\partial\mu_{h}}(\mu_{h} - \mu - \alpha\rho)$$
$$= 1 - \alpha \frac{\partial\rho}{\partial\mu_{h}} = \frac{(\partial p/\partial\rho)_{T}}{(\partial\rho_{h}/\partial\rho)_{T}}.$$
(4.5)

From its definition, λ is a measure of the curvature of V at $\xi = \phi$. It is closely related to the (inverse) correlation length of the liquid. From (4.5) it follows that $0 \le \lambda \le 1$, and that $\lambda \to 0$ as $T \to T_c^-$, $\lambda \to 1$ as $T \to 0$. Note that since M is considered small of second order, it does not affect the linearized equation of motion (4.4).

The general solution of (4.4) can be written as

$$\xi_1 = ae^{\lambda t} + be^{-\lambda t} + ce^{-\beta t} \tag{4.6}$$

with

$$c = -E(1-\beta^2)/(\beta^2-\lambda^2)$$

The constants a and b in the solution of the homogeneous equation associated with (4.4) must be determined by the boundary conditions.

The boundary condition at infinity, $\rho(x \to \infty) = \rho_g$, is now translated into (essentially) an energy condition: In order that the particle ends up on the gas peak with zero energy, the sum of the initial energy and that delivered to the particle by the external force must vanish. Therefore, in general,

$$\frac{1}{2}\dot{\xi}^{2}(0) + V(\xi(0)) + \int_{0}^{\infty} dt \,F(t)\dot{\xi}(t) = 0 \,. \tag{4.7}$$

Within perturbation theory all these quantities are of second order and, at this level of approximation, (4.7) reduces to

$$\frac{1}{2}(\lambda a - \lambda b - \beta c)^2 - \frac{\lambda^2}{2}(a + b + c)^2 + 2\phi M - E(1 - \beta^2) \int_0^\infty dt \ e^{-\beta t} (\lambda a e^{\lambda t} - \lambda b e^{-\lambda t} - \beta c e^{-\beta t}) = 0.$$

$$(4.8)$$

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In writing down (4.8) we have used the fact that the maximum of the liquidlike peak at finite M < 0 is, to leading order, shifted downwards by the amount $2\phi M$.

As long as $\beta > \lambda$ all integrations in (4.8) converge and can trivially be performed. After the algebra has been performed, (4.8) reduces to

$$ab = \frac{\phi M}{\lambda^2} \ . \tag{4.9}$$

Since a and b are small of first order, (4.9) shows that M must be considered a second-order quantity. Equation (4.9) is the energy condition to leading order. It is *almost* equivalent to the corresponding boundary condition at infinity. What is missing is the requirement that $a \leq 0$, i.e., that the motion be asymptotically directed towards the gas peak rather than away from it.

It is important to realize that the straightforward perturbation expansion considered here can only be meaningful for $\lambda < \beta$. Equation (4.5) showed that $\lambda(T)$ ranges from zero at T_c to unity at T=0. Consequently, with $\beta < 1$ and fixed, there is always a low-temperature region in which the restriction $\lambda < \beta$ does not hold. We shall come back to this point.

The boundary condition on the wall, (3.9), or the initial condition in dynamical language, reads

$$\dot{\xi}(0) = \xi(0) - M + \frac{A}{2} - (1+\beta)E$$
 (4.10)

To first order M can be neglected. Introduction of E_0 as given by (3.20) then turns (4.10) into the first-order initial condition

$$\xi_1(0) = \xi_1(0) + 2(E_0 - E) + (1 - \beta)E$$
. (4.11)

With $\xi_1(t)$ given by (4.6) this means that

$$(1-\lambda)a + (1+\lambda)b = \Delta , \qquad (4.12)$$

where

$$\Delta = \frac{1-\lambda^2}{\beta^2 - \lambda^2} (1+\beta)E - 2E_0 \; .$$

For $\beta = 1$ and $E = E_0$, $\Delta = 0$ as it should. When $\beta < 1$, the sign of Δ depends on the relative magnitude of E and $E_0(T)$ (i.e., with fixed ϵ , on T).

Solution of the two equations (4.9) and (4.12) for a and b gives

$$(1+\lambda)b^{\pm} = (1-\lambda)a^{\mp}$$
$$= \frac{1}{2} \left[\Delta \pm \left[\Delta^2 - 4\phi \frac{1-\lambda^2}{\lambda^2} M \right]^{1/2} \right],$$
(4.13)

where upper signs go together. Since $M \le 0$, it follows that $a^+ \le 0$, $b^+ \ge 0$ and $a^- \ge 0$, $b^- \le 0$, regardless of the sign and magnitude of Δ (i.e., regardless of the temperature). But a positive *a* does not represent an acceptable solution to the dynamical problem, since it corresponds to a particle moving off to the right in Figs. 4 and 5 with rapidly increasing velocity,²⁰ i.e., a > 0 violates the boundary condition at infinity, $\rho(x \to \infty) = \rho_g$. Thus only *one* physically acceptable solution (a^+, b^+) exists within the present perturbation treatment.

When M < 0, i.e., $a^+ < 0$, the solution found corresponds to a "particle" which, after some initial hesitation close to the top of the liquid peak, quickly traverses the valley and lands on its gas peak destination. This dynamical picture clearly corresponds to an incompletely wet substrate. No singularities develop as the temperature (i.e., ϵ_0 and λ) is changed.

Complete wetting can, of course, only occur at bulk coexistence. When M=0, already (4.9) shows that either a or b vanishes. By continuity from the (a^+, b^+) solution, a can only be negative and b only positive. Equation (4.12) in that case reduces to

$$\Delta = \frac{1 - \lambda^2}{\beta^2 - \lambda^2} (1 + \beta) E - 2E_0 = \begin{cases} (1 - \lambda)a \\ (1 + \lambda)b \end{cases} .$$
(4.14)

Thus $[a = \Delta/(1-\lambda), b = 0]$ is the only acceptable solution when $\Delta < 0$, whereas $[a = 0, b = \Delta/(1+\lambda)]$ must be chosen when $\Delta > 0$. The first case, $\Delta < 0$, corresponds to incomplete wetting. The second one, $\Delta > 0$, shows a particle that comes exponentially to rest on the liquid peak (from which it crosses over to the gas peak after an indefinite time). This is tantamount to a completely wet surface. The transition between the two cases, at a temperature T_W such that

$$\Delta(T_W) = 0 , \qquad (4.15)$$

is clearly continuous.

We close this section with the following four remarks:

(1) To first order in our perturbation scheme,

Sullivan's conclusion stands up: Even if the range of the substrate potential is made slightly longer than that of the fluid interparticle potential, the wetting transition is continuous and no prewetting is observed. A calculation of competing free energies is not necessary to reach this conclusion, since only one physically acceptable solution exists.

(2) The above certainly holds also to second and, presumably, to higher orders in the present perturbation scheme. However, to go much beyond first order does not make sense, since the expansion used clearly is not a convergent one. (The top of a peak represents an unstable equilibrium point.) It does have an asymptotic meaning, however.

(3) For the present scheme to work, even to first order,²¹ we must require that $\lambda(T) < \beta$. When $\beta < 1$, this leaves open the question of what happens in the low-temperature region where the above requirement is violated. Note that there is no problem in *principle* with the basic equations (4.2) and (4.7) when $\lambda(T) > \beta$. The divergence in (4.8) is clearly an artifact of linearization. Even if simple analytic techniques are not available, the nonlinear problem can therefore be studied numerically. This will be done in future work.

(4) In the linear approximation there is nothing preventing us from taking $\beta > 1$. The results [(4.14) and (4.15)] remain the same; i.e., a sufficiently strong substrate attraction of slightly shorter range than that of the interparticle forces still gives complete wetting and a continuous wetting transition.

V. THE SECOND-PERTURBATION SCHEME

A. The starting point

The calculations of Sec. IV showed that prewetting, if it exists in our model, must be found in the temperature range for which $\beta < \lambda(T)$, i.e., roughly speaking, when the range of the substrate potential exceeds the fluid correlation length. When $\beta < \lambda$, however, the energy condition (4.7) presents an obstacle to analytic progress. To circumvent this difficulty it is tempting to consider the extreme case of $\beta \ll \lambda(T)$. Most of the valley between the liquid and the gas peaks is traversed on a time scale λ^{-1} . On this time scale an external force $\sim e^{-\beta t}$ can be considered a constant, provided that $\beta \ll \lambda$. A constant external force brings us back to (essentially) the problem considered by Sullivan. Unfortunately, we cannot use $\beta \ll \lambda$ directly in the perturbation expansion of Sec. IV, since then the "distance" from Sullivan's case cannot be considered as small.

We can, however, achieve the same benefit by choosing the substrate potential to be

$$\Phi(x) = -\epsilon e^{-x} - \epsilon_{\beta} e^{-\beta x} . \qquad (5.1)$$

The first term, with ϵ close to $\epsilon_0 = (\alpha/2)\rho_l(T)$, cancels identically in the dynamical equation and makes its presence felt in the initial condition only. The second term, with a coefficient $\epsilon_{\beta} = k_B T E_{\beta}$ considered small of second order, contributes an external force

$$F(t) = -E_{\beta}(1-\beta^2)e^{-\beta t} \simeq -E_{\beta}e^{-\beta t}, \qquad (5.2)$$

where we used that $\beta \ll 1$. To leading order this force contributes neither to the dynamical equation nor to the initial condition. It does, however, affect the energy condition.

The choice (5.1) makes it possible to stay close to Sullivan's case and still study the effects of a longrange tail in the substrate potential.

B. Fast solutions

We first search for solutions to the dynamics that represent rapid crossovers from the liquid to the gas peak. Since the first term in (5.1) cancels and the second term is small of second order, the first-order dynamical equation is simply

$$\hat{\xi}_1 - \lambda^2 \xi_1 = 0 \tag{5.3}$$

with solution

$$\xi_1(t) = ae^{\lambda t} + be^{-\lambda t} . \tag{5.4}$$

The energy condition (4.7), if treated in the manner of (4.8), would contain a divergent integral. However, for fast solutions and with $\beta \ll \lambda$, we can consider the external force as a constant, $F \simeq -E_{\beta}$. This constant force will have the same effect on the energy condition as a finite M. Thus the condition becomes, to leading (i.e., second) order,

$$ab = \frac{\phi(M + E_{\beta})}{\lambda^2} . \tag{5.5}$$

The initial condition to first order reads

$$(1-\lambda)a + (1+\lambda)b = \Delta_1, \qquad (5.6)$$

where $\Delta_1 = 2(E - E_0)$ is obtained from the Δ of Eq. (4.14) if one sets $\beta = 1$.

From Eqs. (5.4)–(5.6) it is clear that fast solutions, if they exist, obey to leading order precisely the same equations as those governing Sullivan's case, except that M is replaced by an effective chemical potential, $M + E_B$.

In order to understand the implications of this we use slightly modified versions of Figs. 4 and 5. Figures 7(a) and 7(b) apply to the case when $M + E_{\beta} < 0$, i.e., at some distance below gas-liquid coexistence. The W = 0 trajectory of Fig. 7(b) clearly shows that only one solution with the gas point as



FIG. 7. Potential $V(\xi)$ and W=0 trajectories (solid curves) in the (ξ, ξ) plane are shown for $M+E_{\beta}<0$ in (a) and (b), and for $M+E_{\beta}>0$ in (c) and (d). The dashed lines in (b) and (d) represent initial conditions.

its final destination exists. The wall condition (dashed line) determines the initial point on the trajectory. The situation with $M + E_{\beta} < 0$ is therefore essentially the same as that of Sullivan's case (and that of Sec. IV), with M < 0. Figures 7(c) and 7(d) depict the situation when $M + E_{\beta} > 0$. Since $E_{\beta} > 0$, this includes coexistence, M = 0. From Fig. 7(d) it is clear that, depending on the initial condition (dashed lines), 0, 1, or 2 fast solutions exist. Fast solutions exist only when the dashed line crosses the ξ axis (a finite distance) to the left of $\xi = \phi$, i.e., when $\Delta_1 < 0$. Reference to the expression for the surface free energy in Fig. 6 shows that the solution with the smaller $\xi(0)$ has the lower free energy. Whether this solution is the physical one can only be determined after the possible existence and free energy of slow solutions have been investigated.

Quantitatively, the a's and b's for the fast solutions follow from (5.5) and (5.6) as

$$(1-\lambda)a^{\pm} = (1+\lambda)b^{\pm} = \frac{1}{2}\Delta_{1} \pm \left[\Delta_{1}^{2} - 4\phi \frac{1-\lambda^{2}}{\lambda^{2}} (M+E_{\beta})\right]^{1/2}.$$
(5.7)

For fast solutions to exist, (5.7) shows that one must have

$$4(E - E_0)^2 = \Delta_1^2 \ge 4\phi \, \frac{1 - \lambda^2}{\lambda^2} (M + E_\beta) \,. \tag{5.8}$$

This is trivially fulfilled when $M + E_{\beta} < 0$. In that

case, however, (5.7) shows that $a^- > 0$, and the minus solution must be discarded as unphysical [it corresponds to the upper branch of Fig. 7(b)]. With $M + E_{\beta} < 0$, then, the solution is unique, as indicated by Fig. 7(b).

When $M + E_{\beta} > 0$, (5.8) puts a lower bound on Δ_1^2 , i.e., an upper bound on (the negative²²) Δ_1 . With negative Δ_1 and $M + E_{\beta} > 0$, both a^- and a^+ are negative. Both solutions are therefore physically acceptable. As will become apparent later, the plus solution is the one with lower free energy. This substantiates the picture of Fig. 7.

C. The slow solution

In addition to the fast solutions found above, at least one slow solution must exist for certain ranges of the parameters. [For $\epsilon > \epsilon_0(T)$, the substrate with the potential (5.1) is certainly completely wet at coexistence.]

The dynamics of the slow solution can be pictured as follows (under the assumption that $M + E_{\beta} > 0$). The particle starts moving close to the top of the liquid peak in the tilted potential of Fig. 7(c). The initial conditions are such that it takes a long time τ , of order β^{-1} , for the particle to make the final passage across the top of the peak (with negative velocity). After $t=\tau$, when the tilt of the potential has been reduced to $M + E_{\beta}e^{-\beta t}$, the particle rapidly (on the scale of λ^{-1}) traverses the valley and finds its way to the top of the gas peak.

The first-order condition that the particle passes

the top of the liquid peak at $t = \tau$ reads, from (5.4),

$$\xi_1(\tau) = ae^{\lambda\tau} + be^{-\lambda\tau} = 0.$$
(5.9)

The first-order initial condition is again given by (5.6). With b of first order and $\lambda \gg \beta \sim \tau^{-1}$, the second term in (5.9) becomes small, of much higher order than first order. To leading order [when the particular solution originating in (5.2) is also added to (5.9)], (5.6) and (5.9) therefore give

$$a = -\frac{E_{\beta}}{\lambda^2} e^{-\beta\tau - \lambda\tau} ,$$

$$b = \frac{\Delta_1}{1 + \lambda} ,$$
(5.10)

so that a = 0 to first order. Since (5.10) shows a to be very small and *negative*, this solution is an acceptable one. To first order, however, one should put a = 0.

To make the picture complete, we need an expression for τ . This is furnished by the energy condition. Since for $t > \tau$ the traversal to the gas peak is assumed to be rapid, we can use the same argument as that leading to (5.5) to write the energy condition as

$$\frac{1}{2}\dot{\xi}(\tau)^2 + 2\phi(M + E_{\beta}e^{-\beta\tau}) = 0.$$
 (5.11)

To leading order the kinetic energy is negligible and one finds

$$e^{-\beta\tau} = \frac{-M}{E_{\beta}} . \tag{5.12}$$

Equation (5.11) shows, on the one hand, that a slow solution does not exist when $M + E_{\beta} < 0$. This is as should be expected: Only thin films will form on the substrate for chemical potentials well below coexistence. On the other hand, (5.11) indicates that slow solutions, i.e., thick films, *are* possible close to coexistence when, say, $-M < \frac{1}{2}E_{\beta}$. In particular, as

 $M \rightarrow 0$ one finds $\tau \rightarrow \infty$, corresponding to complete wetting.

The situation is now as follows. We have shown that for $M + E_{\beta} < 0$ no slow solution exists and that, among the two fast ones, only the plus solution is physically acceptable. Conversely, when $M + E_{\beta} > 0$ and $E > E^*$, where from (5.8),

$$E^{*} - E_{0} = \frac{1}{2} \Delta_{1}^{*}$$
$$= - \left[\phi \frac{1 - \lambda^{2}}{\lambda^{2}} (M + E_{\beta}) \right]^{1/2}, \qquad (5.13)$$

and no fast solution exists, whereas a slow one does. The only parameter range in which two solutions compete is thus $M + E_B > 0$, $E < E^*$. The outcome of this competition, which will yield the first-order transition associated with the prewetting line, can only be decided when the free energies associated with the two solutions have been calculated to leading order.

D. The free energy

In the Appendix we sketch derivations of expressions for the first- and second-order shifts in the excess surface free energy associated with perturbations away from the Sullivan model at the temperature where this model has its wetting transition. The first-order shift (A5) is indifferent to the form of the solution $\xi_1(t)$ to the dynamical problem. It is therefore irrelevant to the competition between different solutions of the dynamics. That competition is determined by the second-order shift, given by (A6), or, rather, the difference between the shifts corresponding to the fast and the slow solution. To calculate it, we use (5.7) and discard terms of relative order β/λ . The difference,

$$\Delta\Omega_s / A = \Delta\gamma_{sg} = k_B T(\omega^{f\pm} - \omega^s) ,$$

is, in terms of the original variables, found to be

$$\Delta \gamma_{sg} = \frac{\rho_l - \rho_g}{\kappa \beta} \left\{ \epsilon_{\beta} + \Delta \mu \left[1 + \ln \left[\frac{\epsilon_{\beta}}{-\Delta \mu} \right] \right] \right\} - \frac{\left[\epsilon - \epsilon_0(T)\right]^2}{\kappa \alpha} \frac{2\lambda}{1 - \lambda^2} \left[1 \pm \left[1 - \mu_{hl} \frac{1 - \lambda^2}{\lambda^2} \frac{\Delta \mu + \epsilon_{\beta}}{\left[\epsilon - \epsilon_0(T)\right]^2} \right]^{1/2} \right],$$
(5.14)

Where $\mu_{hl} = k_B T_{\phi}$, $\Delta \mu = k_B T M$. A sketch of $\Delta \gamma_{sg}$ as a function of $[\epsilon - \epsilon_0(T)]$ is given in Fig. 8. Rather than think of T as fixed and ϵ as variable (as we have done in the calculations up to this point), one should keep the potential parameters $\epsilon, \beta, \epsilon_{\beta}$ fixed and vary T—that is, $\epsilon_0(T)$ and $\lambda(T)$. The combination $[\epsilon - \epsilon_0(T)]$ is a monotonically increasing function of T (linear for small $[\epsilon - \epsilon_0(T)]$), and the horizontal axis in Fig. 8 can therefore be regarded as a temperature axis. The solid line corresponds to (5.14), i.e., to use of the plus solution for the fast solution. The dashed line would result if one were to use the minus solution instead.

The fast solutions exist for $\epsilon < \epsilon^* = k_B T E^*$, as given by (5.13). At one particular value of ϵ , which we shall call ϵ_t , $\Delta \gamma_{sg} = 0$. When $\epsilon > \epsilon_t$, $\omega_2^f > \omega_2^s$, the



FIG. 8. Difference $\Delta \gamma_{sg}$ in the excess surface free energy between the fast solution and the slow solution. The solid curve represents the fast plus solution. For comparison the corresponding minus solution is represented by the dashed curve. For $\epsilon > \epsilon_t$ the slow solution has the lower free energy, whereas the fast solution is better when $\epsilon < \epsilon_t$. The first-order phase transition between the two occurs at $\epsilon = \epsilon_t$.

slow solution is the one of physical relevance, and there is a thick film on the substrate. When $\epsilon < \epsilon_t$, on the other hand, the fast solution is better, and the film on the substrate is thin. At $\epsilon = \epsilon_t$ (i.e., at the corresponding temperature) there is a transition between the two. Since the slope of $\Delta \gamma_{sg}$ is finite at $\epsilon = \epsilon_t$, the transition is first order. The prewetting line, defined as the locus of this transition, is given by $\Delta \gamma_{sg} = 0$. For fixed potential parameters this gives an equation for $\Delta \mu_{pw} = \Delta \mu_{pw}(T)$, which applies within the range where our perturbation scheme is valid. Note that the slope, $(d\Delta \mu/dT)_{pw}$, of this line goes to zero as coexistence is approached. From (5.14) one finds that, as $\Delta \mu \rightarrow 0^-$,

$$\frac{d\Delta\mu}{dT}\Big|_{\rm pw} \propto \left|\ln\left(\frac{\epsilon_{\beta}}{-\Delta\mu}\right)\right|^{-1} . \tag{5.15}$$

This is in complete agreement with the thermodynamic result (2.7), for the special case of shortrange (here, exponential) forces.

VI. CONCLUSIONS

In this paper we have shown that prewetting and critical wetting are both within the scope of the lowest-order van der Waals theory of fluids. We are not as yet in a position to formulate general criteria on the substrate and interparticle potentials by which the order of the wetting transition can be determined. Our calculations have so far been restricted to exponential forces. The results of Sec. IV show that, at least within perturbation theory, the wetting transition is continuous as long as $\lambda(T) < \beta$. From Sec. V, on the other hand, one concludes that a long-range [$\beta \ll \lambda(T)$] tail added to the substrate potential produces a first-order wetting transition and prewetting. It is tempting to conjecture that

with exponential forces the range of the substrate potential relative to $\lambda(T)$ is indeed the decisive factor, and that the breakdown of the perturbation theory of Sec. IV at $\lambda(T) = \beta$ signals the crossover to a first-order transition. In Sullivan's model, in which $\beta = 1$, this crossover would then be driven down to zero temperature.

In order to relate to experiments directly, results pertinent to Lennard-Jones—type forces are needed. General statements on nonexponential forces would clearly be premature at this point. We would, however, like to draw attention to Ebner's Monte Carlo results.¹⁰ With a Lennard-Jones (9-3) substrate and nearest-neighbor interparticle interaction, his calculations strongly suggest prewetting for the particular parameters used. If one considers the potentials used in Sec. V as exponential caricatures of those used by Ebner, our results are consistent with his.

Clearly the model calculations for the wetting transition are still in a rather primitive state. Contact with the modern theory of phase transitions and critical phenomena has only recently begun.²³ It is not even clear *a priori* that mean-field—type theories can be trusted to answer the simplest possible question in this context, namely: What is the order of the wetting transition? This paper has been based on the premise that the van der Waals theory *can* be trusted up to this point. If one wants to go beyond it and investigate the nature of the various critical points associated with the wetting transition, mean-field theories are clearly inadequate.

Any microscopic theory, however, must be consistent with thermodynamics. Both van der Waals and more refined theories (if they exist) must yield prewetting lines that are consistent with the Clapeyron equation derived in Sec. II. In particular, the results on the way prewetting line joins the line of bulk coexistence can serve as a check point for future developments.

After the present work was submitted for publication, Tarazona and Evans kindly informed us of their work on the same problem.²⁴ They have made an extensive numerical study of the model treated in Sec. IV. Their results are consistent with ours, and they do find a first-order transition in the region where our first-perturbation treatment does not apply. In addition, the classical Landau phenomenology applicable to the phase diagram of Fig. 1 was worked out by Nakanishi and Fisher.²⁵

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APPENDIX

In this Appendix we sketch the derivation of the expressions for the first- and second-order shifts in the free energy needed in Sec. V. The general expression for the excess surface free energy per unit substrate area, $\gamma_{sg} = \Omega_s / A$, for van der Waals models governed by (3.4) is¹¹

$$\gamma_{sg} = -\frac{1}{2\kappa} \int_0^\infty dx (\{\mu - \mu_h[\rho(x)] - \Phi(x)\}\rho(x) + 2\{p_h[\rho(x)] - p\}).$$
(A1)

Here p is the bulk (gas) pressure, and the prefactor κ^{-1} is due to our choice of measuring x on the scale set by the range κ^{-1} of the forces.

The zeroth-order situation around which we perturb is that of the Sullivan model at gas-liquid coexistence and at the wetting transition point; i.e., $\rho(x) = \rho_l$ for 0 < x < L, where L is a length (unspecified) much longer than the length scales set by the fluid and the substrate potentials. Beyond L there is a liquid-gas interface so that $\rho(x \to \infty) = \rho_g$. The interfacial free energy, which we shall not calculate, is included in γ_{sg} to zeroth order.

We now consider perturbations away from the "Sullivan point," caused by small changes in the substrate potential and by negative shifts in the chemical potential away from its value μ_{gl} at coexistence. To this end we write

$$\Phi(x) = \Phi_0(x) + \delta_1 \Phi(x) + \delta_2 \Phi(x) + \cdots ,$$

$$\mu = \mu_{gl} + \delta_2 \mu + \cdots .$$
(A2)

The shift in $\Phi(x)$ is allowed to be first and/or second order, whereas the shift in μ is considered as second order only.

One now proceeds by expanding (A1) to first order in $\delta_1 \Phi$ and $\delta_1 \mu_h$. Considerable simplification results from use of the zeroth- and first-order versions of the equilibrium conditions (3.4), and from appeal to the symmetry of $\chi(|x-x'|)$. One ultimately finds

$$\delta_1 \gamma_{sg} = \frac{\rho_l}{\kappa} \int_0^\infty dx \, \delta_1 \Phi(x) \; . \tag{A3}$$

Similarly, to second order one finds [this time using (3.4) to second order]

ſ

$$\delta_{2}\gamma_{sg} = -\frac{1}{\kappa} \left[\rho_{l} \int_{0}^{\infty} dx \left[\delta_{2}\mu - \delta_{2}\Phi(x) \right] \right] \\ -\rho_{g} \int_{0}^{\infty} dx \, \delta_{2}\mu \\ -\frac{1}{2} \frac{\partial \rho_{l}}{\partial \mu_{h}} \int_{0}^{\infty} dx \, \delta_{1}\Phi(x) \delta_{1}\mu_{h}(x) \right].$$
(A4)

The expression (A4) does not quite make sense as it stands, since the $\delta_2 \mu$ integrals clearly diverge. The reason for this is that we have made a strict perturbation around $\rho(x) = \rho_l$, although the density, for $\delta_2 \mu < 0$, does cross over to ρ_g at a large but finite distance from the wall. Tracing the origin of the diverging terms, one realizes that, e.g., the first integral in (A4) follows from (A1) after an operation of the type

$$\int_0^\infty dx \left[\mu - \Phi(x)\right] \rho(x) \to \rho_l \int_0^\infty dx \left[\delta_2 \mu - \delta_2 \Phi(x)\right] \,.$$

In view of the ultimate crossover to ρ_g it is more reasonable (if less rigidly systematic) to keep the x dependence of $\rho(x)$ in terms involving the constant shift $\delta_2 \mu$ and the very slowly varying $\delta_2 \Phi(x)$ ($\sim e^{-\beta x}$ in Sec. V). With the potential (5.1) the dimensionless shifts $\delta_n \gamma_{sg}/k_B T = \omega_n$ then become

$$\omega_{1} = -\frac{\rho_{l}}{\kappa} (E - E_{0}) \int_{0}^{\infty} dt \, e^{-t}$$

$$= -\frac{\rho_{l}}{\kappa} (E - E_{0}) , \qquad (A5)$$

$$\omega_{2} = -\frac{1}{\kappa} \int_{0}^{\infty} dt \left[M[\rho(t) - \rho_{g}] + E_{\beta} \rho(t) e^{-\beta t} + \frac{1}{2} \frac{1 - \lambda^{2}}{A} (E - E_{0}) e^{-t} \xi_{1}(t) \right] . \qquad (A6)$$

This expression is the basis for the discussion of the competing solutions found in Sec. V.

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- ¹⁶This is a consequence of the particle-hole symmetry of the lattice gas or, equivalently, of the magnetic symmetry in the corresponding Ising model.
- ¹⁷Any short-range repulsion will do, but for simplicity we use a hard-core reference system.
- ¹⁸N. G. van Kampen, Phys. Rev. <u>135</u>, A362 (1964).
- ¹⁹This result is valid for any model for μ_h, p_h (see Ref. 11).
- ²⁰The minus solution cannot be accepted in the context of wetting, where the boundary condition is $\rho(x \to \infty) = \rho_g$. It does, however, have a physical meaning in the corresponding problem of drying, where $\rho(x \to \infty) = \rho_l$. For that problem the plus solution is unacceptable.
- ²¹Higher-order terms have progressively restricted ranges of validity.
- ²²The whole W = 0 trajectory with $\Delta_1 > 0$ lies to the right of $\xi = \phi$ in Fig. 7(d). It does not connect to the gas point and must be discarded.
- ²³Exponents associated with critical wetting of a threedimensional system are calculated by D. M. Kroll and R. Lipowsky, Phys. Rev. B <u>26</u>, 5289 (1982).
- ²⁴P. Tarazona and R. Evans, Mol. Phys. (in press).
- ²⁵H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. <u>49</u>, 1565 (1982).