

Critical wetting of surfaces in systems with long-range forces

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We solve the mean-field equations for a lattice gas in the presence of a substrate. All forces in the system are long ranged. We show that, for a suitable choice of potentials, critical wetting can occur and we observe it explicitly for the first time. This contrasts with all previous calculations and with claims in the literature that first-order wetting is generic.

The nature of the different kinds of wetting transitions which are possible has become of increasing interest,¹⁻¹² particularly in light of the several experiments recently undertaken to study this transition.¹³ There is little doubt that a first-order wetting transition can occur. In such a case, the excess surface density n_s adsorbed on the walls of a container enclosing a gas at two-phase coexistence jumps discontinuously from a finite to an infinite value as the temperature T is increased. The observation of the analogous first-order transition in binary liquid mixtures has been reported.¹⁴ The possibility of a continuous transition, denoted critical wetting, is less clear. If all forces in the system were of short range, critical wetting could occur and the fluctuations of the adsorbed film would be crucial to the critical properties.² However, it was found in a solid-on-solid model that, in the presence of long-range forces of the kind to be expected in experiment, the fluctuations of the interface were unable to bring about a wetting transition at all. The only wetting transitions observed were first-order ones which are not brought about by fluctuations.³ Thus, in contrast to models with short-range forces, fluctuations are not important to the nature of the wetting transition with the consequence that mean-field theory (MFT) should provide an adequate description. Further support for this view can be obtained from Ref. 3(b) from which the upper critical dimension can be obtained. In this paper, the MFT values of the critical exponents α and ν are given for the case in which all forces are long ranged and the surface free energy of a system with excess surface density n_s varies, for large n_s , like a/n_s^σ ($\sigma=2$ for van der Waals forces) plus higher-order corrections of arbitrary power b/n_s^τ . From these exponents and the fact that hyperscaling should hold at d^*-1 , where d^* is the dimension of the bulk at the upper critical dimension of the wetting transition, one obtains $d^*=3-4/(\tau+2)$ which is less than three.⁴ Thus, provided only that the wetting transition does not occur within the bulk critical region, MFT is expected to yield the correct critical behavior in three dimensions for the wetting of a substrate-vapor interface.

Even within the context of MFT, the existence of critical wetting cannot be established unless the kind of system in which it is likely to be found is known. This question can be studied by constructing a surface free energy per unit area, $f_s(n_s, T)$, and the ancillary function $\hat{\Omega}_s(n_s, T) = f_s(n_s, T) - \mu_0 n_s$ with $\mu_0(T)$ the chemical potential at coexistence. The value of n_s at coexistence occurs at the minimum of $\hat{\Omega}_s$.

If this minimum occurs at a finite n_s the system is not wet; if it occurs at an infinite n_s , the system is wet. Much

about the possible wetting behavior can be inferred from an expansion of $\hat{\Omega}_s$ for large n_s . It is convenient to express $\hat{\Omega}_s$ in terms of $\psi \equiv n_s^{-1} \geq 0$. Thus,

$$\hat{\Omega}_s(\psi, T) = \hat{\Omega}_s(0, T) + a(T)\psi^2 + b(T)\psi^3 + \dots + \dots, \quad (1)$$

where the leading ψ^2 behavior arises from van der Waals forces,⁵ and not for reasons of symmetry. When the system is wet, $a(T)$ is positive and the global minimum occurs at $\psi=0$. As usual, there are two mechanisms by which this global minimum can shift to a nonzero value of ψ which represents a system that is not wet. The first occurs because $b(T)$, or the coefficient of a higher-order term, is negative causing a local minimum at nonzero ψ . As the temperature is lowered, this local minimum becomes the global one and a first-order transition occurs. At this transition, $a(T)$ is still positive. The mechanism occurs *inter alia* in models in which the only forces that are long range are those between adsorbate and substrate.^{6,11} In such models, $a(T)$ is always positive. [See Eq. (3) below.] The second mechanism can occur if $b(T)$ is positive and $a(T)$ can change sign from positive to negative as the temperature is decreased. That $a(T)$ can change sign was recently shown to be plausible.⁷ Then a critical wetting occurs at T_w , where $a(T_w)=0$, and the excess surface density diverges like $(T_w - T)^{-1}$ as T_w is approached from below.^{3(b)} Thus, it appears that critical wetting in a system with long-range forces could occur.

In light of this expectation it is a surprise that of three MFT calculations which have been carried out on systems in which all potentials are long-range Lennard-Jones 6-12, *all of them* report first-order wetting transitions *only*.⁸⁻¹⁰ Indeed, it has been suggested^{3(a),10,15} that this behavior is generic.¹⁶ Spurred by the disagreement between our expectations and these results, we have carried out an MFT calculation on a lattice-gas model of absorption^{1,9,12} in which all potentials are long ranged. However, we have been guided in our choice of potentials by an approximation to the free-energy function $\hat{\Omega}_s(n_s, T)$. As a consequence, we have found, for the first time, critical wetting in such a model system with long-range forces.

We have considered the lattice-gas Hamiltonian

$$H = \frac{1}{2} \sum_{i \neq j} v_{ij} c_i c_j + \sum_l [u(l) - \mu_0] c_l$$

on a cubic lattice with unit lattice constant where the occupation variables $c_l = 0$ or 1, and l is the distance of the i th site from the substrate. We take the substrate-adsorbate in-

teraction $u(l)$ to depend on this distance only and to have the asymptotic form, for large l , $u(l) \rightarrow -u_3 l^{-3} - u_4 l^{-4} + \dots$, with u_3 positive. The interaction v_{ij} is between two particles only. To facilitate comparison with $u(l)$, it is convenient to construct the interaction $v(m) = v(|m|)$ between an atom and a plane of adsorbate atoms a distance $|m|$ from it, $v(m) = \sum_j v_{ij}$ with i and j contained in planes parallel to the substrate a distance $|m|$ apart. From this, the interaction $t(l)$ between an atom and a semi-infinite substrate composed of adsorbate atoms is constructed:

$$t(l) = \sum_{m=1}^{\infty} v(m) ,$$

with asymptotic form at large l , $t(l) \rightarrow -t_3 l^{-3} - t_4 l^{-4} + \dots$, with t_3 positive. The MFT equations are

$$\Delta n = \tanh(T_c \Delta n / T) ,$$

with T_c , the bulk transition temperature, given by

$$k_B T_c = -\frac{1}{4} \sum_{m=-\infty}^{\infty} v(m) \quad (2)$$

and $\Delta n = n_G - n_L$, the difference in the densities of the coexisting bulk liquid and gas, and

$$M(l) = \tanh \left[\left(h(l) - \frac{1}{4} \sum_{m=1}^q v(l-m) M(m) \right) / k_B T \right] ,$$

where the average value of the variable c_l in a plane a distance l from the substrate is $[1 + M(l)]/2$, and where

$$h(l) = \frac{1}{2} \left[\frac{1}{2} t(l) - u(l) - \frac{\Delta n}{4} \sum_{m=q+1}^{\infty} v(l-m) \right] .$$

The excess surface density n_s is then

$$n_s = \sum_{l=1}^{\infty} \left\{ \frac{1}{2} [1 + M(l)] - n_G \right\} .$$

Note that we have replaced $M(m)$ by its bulk value Δn for m greater than a cutoff q which was usually taken to be 80.

To obtain guidance as to a potential which might favor critical wetting, we examined the following sharp-kink approximation to $\hat{\Omega}_s(n_s, T)$:

$$\hat{\Omega}_s \equiv [F(\{n_i^*\}, T) - F(\{n_G\}, T)] / A ,$$

where A is the substrate area, and

$$F(\{n_i\}, T) = \frac{1}{2} \sum_{i \neq j} v_{ij} n_i n_j + \sum_i [u(l) - \mu_0(T)] n_i + k_B T \sum_i [n_i \ln(n_i) + (1 - n_i) \ln(1 - n_i)] ,$$

and $n_i^* = n_L(T)$ if the distance from i to the substrate is less than or equal to l and $n_i^* = n_G(T)$ otherwise. The excess surface density is $(n_L - n_G)l$. The asymptotic form of this function is the same as Eq. (1) but with $a(T)$ replaced by

$$\bar{a}(T) = -(n_L - n_G)^3 (t_3 n_L - u_3) / 2 , \quad (3)$$

which is of the form obtained in Ref. 7, and

$$\bar{b}(T) = (n_L - n_G)^4 [(t_3 - \frac{2}{3} t_4) n_L - (u_3 - \frac{2}{3} u_4)] / 2 .$$

Because n_L decreases from 1 to $\frac{1}{2}$ as T increases from 0 to T_c , $\bar{a}(T)$ can change sign from negative to positive at the

temperature T_w given by

$$n_L(T_w) = u_3 / t_3 \quad (4)$$

provided that

$$\frac{1}{2} < (u_3 / t_3) < 1 . \quad (5)$$

At this temperature the sign of $\bar{b}(T)$ is positive or negative according to whether (t_4 / t_3) is less than or greater than (u_4 / u_3) . Thus, we choose a potential for which Eq. (5) is satisfied and for which

$$t_4 / t_3 < u_4 / u_3 . \quad (6)$$

In particular, we have solved the MFT equations with

$$v(m) = -\epsilon (c_1 m^{-4} + c_2 |m|^{-5}), \quad m = \pm 1, \pm 2, \dots , \\ = -\epsilon c_3, \quad m = 0 ,$$

and

$$u(l) = -\epsilon (c_4 l^{-3} + c_5 l^{-4}), \quad l \geq 2 , \\ = -\epsilon c_6, \quad l = 1 ,$$

with $c_1 = 0.7$, $c_2 = 0.3$, $c_3 = 1.4$, $c_4 = 0.2$, $c_5 = 0.6$, and $c_6 = 1$. For these potentials, Eq. (2) yields $k_B T_c / \epsilon = 0.88$, $u_3 / t_3 = 0.86$, and $t_4 / t_3 = 1.82 < u_4 / u_3 = 3$. In order to determine the absolute minimum of the MFT surface free energy, an accuracy of a part in 10^{+10} was necessary in the difference of this free energy evaluated for nearby solutions of the MFT equations. The size of the cutoff was chosen so that its effect on this difference was less than one part in 10^{+12} .

The excess surface density obtained for this potential is shown in Fig. 1 plotted versus $t \equiv (T_c - T) / T_c$. After a smooth increase to two layers followed by a jump to eight

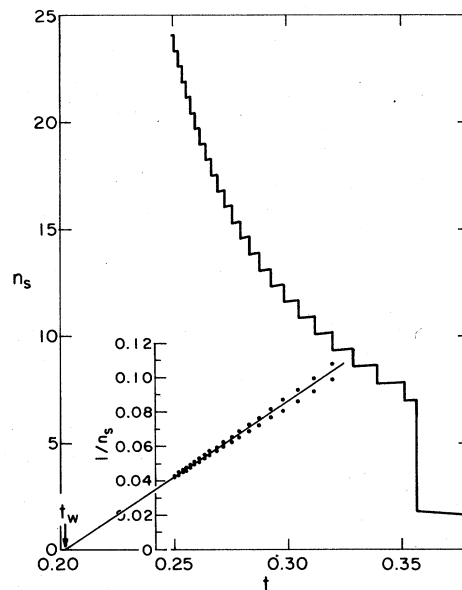


FIG. 1. Excess surface density and its inverse plotted vs reduced temperature $t = (T_c - T) / T_c$ where T_c is the bulk critical temperature.

layers, n_s increases via a sequence of single-layer transitions. We have followed them to 31 layers. We also show in Fig. 1 the same data plotted in the form of n_s^{-1} vs t . The extremes of each step are shown as points and the solid curve is drawn through their average. That the solid curve is linear shows that the excess surface density diverges as $(T_w - T)^{-1}$, precisely the form expected from critical wetting. The sequence of discrete layer transitions is, of course, a consequence of the lattice-gas model and the use of MFT. This would be absent in a discrete model above the roughening temperature and also in a continuum model. The critical wetting temperature T_w is that given by Eq. (4).

We conclude, therefore, that critical wetting *can* occur in systems with long-range forces. For it to occur, however, it is not sufficient that the relative strengths of the leading terms of the substrate-adsorbate to adsorbate-adsorbate potentials, u_3/t_3 , be sufficiently small [Eq. (5)]. It appears that restrictions on the amplitudes of the next-to-leading terms must also be fulfilled [Eq. (6)]. These amplitudes, which are affected by many-body forces and substrate structure, are not known at present for any real system. Our conclusions are not necessarily in conflict with the results of previous studies^{8-10,15} which employed integrals of pure Lennard-Jones 6-12 potentials for the interactions u and t , but do conflict with the inference drawn in some of them that the first-order transitions obtained there were generic. We note that the use of these particular potentials entails a specific choice of the expansion coefficient $b(T)$ in Eq. (1), a choice which is obviously not unique.

For completeness, we note that we have studied a system with the same potentials as reported above with the single exception that c_5 in $u(l)$ was changed to 0.2. In this case, $t_4/t_3 = 1.82 > u_4/u_3 = 1$. We found that n_s increased

smoothly with temperature up to the value 4.81 at $t = 0.15$. At this point, a first-order wetting occurred, which is consistent with the fact that Eq. (6) is not fulfilled. Were the potential of a real system known, including its next-to-leading corrections, the same calculation we have carried out for two cases above could be repeated to determine the order of the wetting transition in that system.

In summary, we have studied a lattice model of a gas which is just at liquid-vapor coexistence and which is in contact with a substrate. All forces in the model were taken to be of the long-range form expected in real systems. We observed, for the first time, the occurrence of critical wetting in which the excess surface density diverges as $(T_w - T)^{-1}$. There is no reason why such a transition could not be observed in experimental systems. Our calculation shows that the nature of the wetting transition in a given adsorbate-substrate system is more subtle than previously supposed. Any *ab initio* calculation to determine that nature for a specific system must, correspondingly, be more detailed. First, the wetting transition depends on the long-range behavior of both substrate-adsorbate and adsorbate-adsorbate forces, so that it is not adequate to truncate the later as in square-gradient approximations.¹⁷ Second, the transition depends in particular on the next-to-leading order terms in these expansions⁷ which are affected by many-body forces and the nature and structure of the substrate. Thus, it is not adequate to approximate these potentials by structureless integrals of pair potentials. In view of the present ignorance of real potentials, the nature of the wetting transition is an open question to be experimentally resolved.

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