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Elusiveness of the prewetting transition

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Although prewetting transitions have been predicted to be present in systems showing first-order wetting transitions, they have to date proved to be difficult to detect. Using an Ising lattice-gas model, we give qualitative predictions of the intervals of chemical potential (or pressure) and temperature over which the prewetting transition may be found for various adatom-adatom and adatom-substrate potentials, including the physically realistic case of van der Waals interactions.

Prewetting transitions were predicted[1,2] to be present in systems with first-order wetting transitions. Although several such wetting transitions have been reported,[3-5] the associated prewetting transitions, with one possible exception,[6] have not been found. It has been suggested[7] on the basis of model calculations that the reason for the elusiveness of prewetting transitions is that they lie so close to the adsorbate bulk transition as to render them difficult to detect and/or identify separately. In this paper we present detailed results of calculations using an Ising lattice-gas model in which the prewetting line was studied as a function of the relative properties of the adatom-adatom and adatom-substrate interactions.

To begin, we consider the physisorption of a phase α on a substrate γ beneath an "atmosphere" β with which, at temperature T, α coexists when the chemical potential μ equals $\mu_0(T)$. Thus $\mu_0(T)$ defines the α-β coexistence line in the μ-T plane. Suppose further that there is a first-order wetting transition at the point $[T_w, \mu_w = \mu_0(T_w)]$. Then there will be a line of first-order, prewetting (PW) transitions extending away from (T_w, μ_w) into the region of stable β; let this line be given by $\mu_p(T) = \mu_0(T) + \Delta\mu_p(T)$. A schematic phase diagram is shown in Fig. 1. The PW transition is marked by a discontinuity in the coverage, or excess surface density Γ, defined by

$$\Gamma \equiv \int_0^\infty dz[n(z) - n_\beta] , \tag{1}$$

where $n(z)$ is the density (or appropriate generalization) a distance z from the substrate and n_β is the density in the bulk β phase. In case of variations in density lateral to the substrate, $n(z)$ and n_β are the densities after averaging over the lateral directions. The line of PW transitions ends at a prewetting critical point $(T_{\rm cpw}, \mu_{\rm cpw})$ where the discontinuity in Γ vanishes.

For the investigations of the PW line reported here, we have used an Ising model[8,9] on a simple cubic lattice with a [100] direction normal to the substrate which occupies the domain $z \leqq 0$. Two distinct types of potentials were studied. In the first, the substrate was considered to be composed of atoms on the sites of the lattice at $z \leqq 0$. A substrate atom and an adatom interact via a pair potential $v(r)$ where r is the interparticle separation. Similarly, two adatoms interact via a potential $u(r)$. The total substrate potential V_k acting on an adatom k layers from the substrate is thus the sum of $v(r)$ over all sites at $z \leqq 0$. It is useful to define an analogous potential W_k found by summing $u(r)$ over all sites at $z \leqq 0$; i.e., W_k would be the substrate potential if the substrate were composed of adatoms. Finally, let us also define $w_k \equiv W_k - W_{k+1}$, which is the interaction energy of an adatom with a layer of adatoms at a distance ka; w_0 will be taken as the interaction of an adatom with all other adatoms in the same layer.

The set of interactions used in this first case is as follows:

$$u(r) = \begin{cases} J[(a/r)^{12} - 2(a/r)^6], & r \leqq r_0 \\ 0, & r > r_0 \end{cases} \tag{2}$$

$$v(r) = RJ[(a/r)^{12} - 2(a/r)^6] . \tag{3}$$

Both u and v are Lennard-Jones (6-12) interactions except that $u(r)$ is cut off at r_0. The minimum of each potential is at $r = a$, the lattice constant, and they have depths of J and RJ, respectively. We have examined the prewetting line, both in mean-field theory (MFT) and Monte Carlo (MC) simulations for a variety of values of r_0 in order to

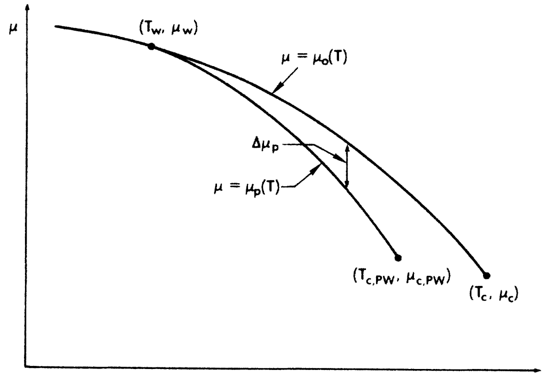

FIG. 1. Typical gas-liquid phase coexistence line $\mu = \mu_0(T)$ in T-μ space with a first-order wetting transition at (T_w, μ_w) and a prewetting line ending at the prewetting critical point $(T_{\rm cpw}, \mu_{\rm cpw})$.

TABLE I. Prewetting critical points in the mean-field approximation using potentials specified by Eqs. (2) and (3). The wetting temperature T_w is $T_c/2$.

r_0/a	R	k_BT_w/J	$(T_{\rm cpw}-T_w)/T_c$	$10^3(\mu_0-\mu_{\rm cpw})/k_BT_c$
1	0.31	0.75	0.31	30
2	0.6936	1.197	0.26	27
3	0.8302	1.289	0.22	15
4	0.8726	1.308	0.20	11
5	0.8982	1.317	0.16	5.2
6	0.9133	1.320	0.155	3.3
8	0.9270	1.323	0.145	1.8
10	0.9344	1.324	0.137	0.95
15	0.9591	1.325	0.071	0.32
20	0.9568	1.325	0.053	0.14
25	0.9692	1.325	0.040	0.069
30	0.9711	1.325	0.033	0.037

determine its behavior as a function of the relative range of u and v. For each value of r_0, R was adjusted so that, in the mean-field approximation, the wetting transition temperature T_w is $T_c/2$ where T_c is the bulk critical temperature, $k_BT_c=-(w_0/2+W_1)/2$. For $r_0<\infty$, this transition is first order, becoming continuous in the limit $r_0\rightarrow\infty$.

Table I shows the results of MFT calculations[8] for a variety of r_0/a. We tabulate both $(T_{\rm cpw}-T_w)/T_c$ and $|\mu_{\rm cpw}-\mu_0|/k_BT_c$ as well as T_w itself. Note that in our model $\mu_0=w_0/2+W_1$, independent of T. In these calculations we have identified the prewetting critical point as that point where the discontinuity in coverage at the prewetting transition has decreased to a monolayer of atoms or less. This procedure is necessitated by the presence of layering transition (whose importance is exaggerated by the mean-field approximation) in the lattice model; such transitions are not expected to be in fluid films except possibly close to the substrate. From Table I we can see clearly that as the range r_0 of $u(r)$ increases, the prewetting line shrinks in length with the prewetting critical point approaching the wetting transition point. The deviation of $\mu_{\rm cpw}$ from μ_0 rapidly becomes very small as the prewetting line shrinks. Such behavior is expected in light of the fact that the prewetting line and bulk coexistence line have a common tangent at the wetting transition point.[10]

Monte Carlo simulations, following the standard algorithm of Metropolis *et al.*,[11] were undertaken as an independent check on the MFT results. Because of the large amount of computer time necessary to do simulations in systems with long-range adatom-adatom interactions, we resorted to a hybrid scheme, combining Monte Carlo and mean-field methods, for $r_0>4a$. The method is as follows: When finding the energy change accompanying the addition or removal of a given adatom during a particular pass through the lattice, we sum explicitly over the interactions of the adatom with all others within a distance l; those beyond this distance are accounted for by a mean field in that each site at $r>l$ is supposed to be occupied with a probability P_k depending on the layer k in which the site resides. Each P_k is set equal to the mean occupation number in layer k at the end of the previous pass through the lattice. In practice we used $l=3a$, and so employed the hybrid method for $r_0/a\geqq 4$. For the particular case of $r_0/a=4$, both the hybrid and standard Monte Carlo methods were used and the results compared. The surface phase diagrams, in particular the prewetting critical points, were identical within statistical uncertainties resulting from the Monte Carlo method itself.[11,12]

We employed a lattice of 15 layers and measuring 40×40 in a plane at constant k. To account for interactions of adatoms with particles in layers beyond the fifteenth one, we again used a mean field assuming $P_k=n_\beta$ for $k>15$. The results for $\Delta\mu\equiv\mu_0-\mu_{\rm cpw}$, in units of the mean-field bulk critical temperature, are given in Table II. In units of the true critical temperature it would be some 25% larger. The qualitative trend of $\Delta\mu$ as a function of r_0/a is the same as in the MFT results. We estimate the uncertainty in $\mu_{\rm cpw}/k_BT_c$ to be about 10^{-3}. We did not consistently calculate $T_{\rm cpw}-T_w^*$, where T_w^* is the MC wetting transition temperature. From our limited work we infer that this temperature difference is generally rather smaller than predicted by MFT; one would expect as much since fluctuations should depress the prewetting critical temperature more than the temperature of the first-order wetting transition.

The second type of potential employed[13] is such that both u and v have $1/r^6$ behavior at large r but differ in

TABLE II. Prewetting critical points from Monte Carlo simulations using potentials specified by Eqs. (2) and (3).

r_0/a	R	$10^3(\mu_0-\mu_{\rm cpw})/k_BT_c$
1	0.31	20
2	0.6936	21
3	0.8302	15
4	0.8726	10
5	0.8982	6.1
6	0.9133	4.0
8	0.9270	2.9
10	0.9344	2.0

TABLE III. Prewetting critical points in MFT using potentials specified by Eqs. (4) and (5) with $\gamma_p=0$ for $p>4$ and $R=0.99$.

γ_4	T_w/T_c	$(T_{\rm cpw}-T_w)/T_c$	$10^3(\mu_0-\mu_{\rm cpw})/k_BT_c$
−0.02	0.4866	0.0077	0.074
−0.04	0.5426	0.0124	0.190
−0.06	0.5879	0.0173	0.312
−0.08	0.6265	0.0212	0.430
−0.10	0.6606	0.0235	0.528
−0.12	0.6913	0.0244	0.600
−0.14	0.7194	0.0240	0.635
−0.16	0.7451	0.0230	0.643

their shorter-range behavior. The calculations were done using MFT, in which case only w_0, W_k, and V_k are needed. These were taken as

$$W_k=-J/k^3 \quad (w_0=-2J)\ , \tag{4}$$

$$V_k=-RJ\left[1/k^3+\sum_{p\geq 4}\gamma_p/k^p\right]\ . \tag{5}$$

This choice is based on the observation that if $w(r)\sim v(r)\sim r^{-6}$ at large r, then W_k and V_k have leading terms at large r proportional to k^{-3}. Because only the relative behavior of W_k and V_k is of primary importance in determining the adsorption phase diagram,[9,14] Eqs. (4) and (5) are sufficiently general to study the systematics of the prewetting line with van der Waals forces present. As described in Ref. 9, if all γ_p are zero with $\frac{1}{2}<R<1$, fourth-order critical wetting results in MFT;[15] if the γ_p's are predominantly negative, first-order wetting occurs; if positive, critical wetting is the outcome. Tricritical and critical end-point wetting transitions also take place for special sets of γ_p's, and wetting can be suppressed altogether for sufficiently negative (repulsive) values of these coefficients. In view of the fact that first-order wetting appears to be most common in nature, we may surmise that taking W_k and V_k as in Eqs. (4) and (5) with, e.g., $\gamma_4<0$ and $\gamma_p=0$, $p>4$, provides a plausible model for studying systems with van der Waals forces. Table III presents results for the prewetting critical point at $R=0.99$ and various $\gamma_4<0$. For $\gamma_4=0$ there is, of course, no prewetting line as there is a fourth-order critical wetting transition here. Then as γ_4 is made increasingly negative, the prewetting line grows but does not become very extensive in that $(T_{\rm cpw}-T_w)/T_c$ is never more than about 2.5%. For more negative γ_4 than shown in the table, the line actually shrinks again as T_w rises to T_c and $T_{\rm cpw}$ is never larger than T_c unless there is an enhancement in the coupling between adatoms close to the substrate.[9,16] Further, as for the first set of potentials, we see that the prewetting line lies very close to the bulk coexistence line.

Next we turn to the implications of these results regarding experimental observation of the PW transition. We have found that when the ranges of u and v are comparable, as they are in many experimentally accessible systems, then the prewetting line exists over a range of temperatures on the order of 2% of the bulk critical temperature and, perhaps even more discouraging, that it lies at a chemical potential which differs from that of the bulk transition by an amount on the order of $10^{-3}k_BT_c$. From the Gibbs-Duhem relation this last figure predicts

$$P_0-P_{\rm cpw}\simeq n_0k_BT_c[(\mu_0-\mu_{\rm cpw})/k_BT_c]$$
$$\sim 10^{-3}n_0k_BT_c\ ,$$

where n_0 and P_0 are, respectively, the density and pressure of the β phase at bulk coexistence and $p_{\rm cpw}$ is the pressure at the critical prewetting point. Although the Ising model is certainly not a quantitatively reliable guide to the properties of fluids, we do feel that our results are qualitatively sensible and are consistent with the lack of experimental observations of the prewetting transition except for the work reported in Ref. 6. However, since that work dealt with a mixture (2-6-lutidine and water) which has an inverted bulk fluid phase coexistence curve and consolute point, it is not inconceivable that its properties are quite different from those predicted by our model. In any event, a prewetting line much longer than the ones found here is reported in Ref. 6.

One shortcoming of our model is that it does not allow for substantial variation of the adsorbate density close to the substrate which would be present in a fluid close to a hard wall. As shown recently by Freasier and Nordholm,[17] such structure can have an effect on the line of prewetting transitions; in particular, the line can be lengthened by a significant amount. Our results are therefore probably more nearly applicable to the case of a soft substrate, such as a liquid or vapor, which would produce much less structure in the density of the adsorbate. This latter type of system is, of course, just what was employed in the experiments of Schmidt and Moldover.[5]

Finally, we note that wetting transitions have typically been observed in binary liquid mixtures, α and β being distinct liquid phases, whereas the model investigated here has been interpreted as a liquid-gas system comprised of a single chemical component. It may also be interpreted as a very simple model of a binary fluid mixture in which μ plays the role of the difference between the chemical potentials of the two chemical species, aside from an additive constant. In this case also $P_0-P_{\rm cpw}$ will be

$10^{-3} n_0 k_B T_c$, where n_0 is the difference of the densities of the chemical components in the β phase and T_c is the temperature of the consolute point.

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[1] C. Ebner and W. F. Saam, Phys. Rev. Lett. **38**, 1486 (1977).

[2] J. W. Cahn, J. Chem. Phys. **66**, 3667 (1977).

[3] M. R. Moldover and J. W. Cahn, Science **207**, 1073 (1980).

[4] D. W. Pohl and W. I. Goldberg, Phys. Rev. Lett. **48**, 1111 (1982).

[5] J. W. Schmidt and M. R. Moldover, J. Chem. Phys. **79**, 379 (1983).

[6] D. Beysens and D. Estève, Phys. Rev. Lett. **54**, 2123 (1985).

[7] R. Evans and P. Tarazona, Phys. Rev. A **28**, 1864 (1983).

[8] The model and mean-field theory are the same as used in Ref. 9 and will not be described in detail here.

[9] C. Ebner, W. F. Saam, and A. K. Sen, Phys. Rev. B **31**, 6134 (1985); **32**, 1558 (1985).

[10] E. H. Hauge and M. Schick, Phys. Rev. B **27**, 4288 (1983).

[11] N. Metropolis, A. W. Rosenbluth, M. N. Rosenbluth, A. H. Teller, and E. Teller, J. Chem. Phys. **21**, 1087 (1953).

[12] We did not attempt to compute any critical exponents; these would presumably not be given correctly by the hybrid method.

[13] These potentials were used extensively in Ref. 9.

[14] A. K. Sen, Ph.D dissertation, Ohio State University, 1985.

[15] The same is found using Eqs. (2) and (3) with $r_0 \rightarrow \infty$, consistent with the claim that only the relative behavior of u and v is important.

[16] H. Nakanishi and M. E. Fisher, Phys. Rev. Lett. **49**, 1565 (1982).

[17] B. C. Freasier and S. Nordholm, Mol. Phys. **54**, 33 (1985).