PHYSICAL REVIEW A VOLUME 23, NUMBER 4 APRIL 1981

Evidence for the roughening and wetting transitions in the lattice-gas model of adsorption from Monte Carlo simulations

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(Received 23 October 1980)

The formation of a dense adsorbed film on a smooth substrate is studied via Monte Carlo simulations of a lattice gas with nearest-neighbor interactions. The existence of the wetting transition which is predicted by a simple mean-field approximation is verified. We also find the sequence of first-order transitions which appear in the mean-field approximation. In contrast to the predictions of the mean-field approximation, the critical temperatures of these transitions appear to approach a limiting value well below the critical temperature of the bulk three-dimensional lattice gas as the thickness of the adsorbed film increases. This behavior, which was first predicted on physical grounds by de Oliveira and Griffiths, is presumably closely related to the roughening transition of the interface between the dense and tenuous bulk phases.

I. INTRODUCTION

The lattice-gas model of adsorption has been explored in a simple mean-field approximation by de Oliveira and Griffiths[1] and more recently by Ebner.[2] One interesting conclusion of these investigations is that for appropriately chosen interactions in the gas and between the gas and substrate, one may obtain no wetting, partial wetting, or complete wetting of the substrate, depending on the value of the temperature T. In this context we mean by "wetting" the appearance of a dense adsorbate or film on the substrate at chemical potentials and temperatures such that the stable bulk phase is a dilute one, i.e., a gas. By "complete wetting" we mean that the adsorbed film grows either continuously or in one-layer steps as the chemical potential μ is increased from $-\infty$ to that value at which the dense bulk phase forms; "partial wetting" means that the coverage first jumps from a fraction of a layer to several or many layers (depending on T) and then grows either continuously or in one-layer steps as μ increases; and "no wetting" means that the coverage remains a fraction of a layer until μ reaches that value at which the dense bulk phase forms. As T rises from zero, the system passes through the nowetting, partial-wetting, and complete-wetting regimes in that order. This phase transition is an example of the wetting transition predicted from general arguments by Cahn[3] and from a density-functional theory of classical liquids by Ebner and Saam.[4] Other recent papers presenting thermodynamic arguments which give qualitatively some of the possible behaviors of adsorption isotherms are those by Dash[5] and Peierls.[6] To the best of the author's knowledge, the paper of Dzyaloshinskii *et al.*[7] was the first in the modern literature to present a complete catalog of possible adsorption isotherms for a fluid on a solid substrate.

A second product of the mean-field calculations is the prediction of the first-order phase transitions, mentioned in the preceding paragraph, in each of which the coverage or adsorbate thickness changes by approximately one layer. According to these calculations and for suitable potentials there seem to be an infinite number of transitions. Each has its own critical temperature T_{cj}, $j = 1, 2, \ldots$; it is convenient, although not completely precise, to think of the jth transition as the addition of the jth layer to the adsorbed film. Within the mean-field approximation the T_{cj} appear to approach T_3, the critical temperature of the three-dimensional lattice gas as j becomes large, and T_2, the critical temperature of the two-dimensional net formed by a single layer of the lattice, for $j=1$. de Oliveira and Griffiths[1] have pointed out, however, that the first of these predictions is likely to be a spurious consequence of the mean-field approximation and that the T_{cj}'s will probably remain below and perhaps approach as $j \to \infty$ the temperature T_R of the roughening transition originally suggested by Burton and Cabrera[8] to exist in surfaces such as that between the bulk phases of the lattice gas. The existence of such transitions has been confirmed both theoretically[9] and experimentally.[10]

The present work was undertaken in an attempt to determine whether the wetting transition arising from mean-field calculations is indeed a property of the lattice-gas model of adsorption and also to determine the correct behavior of T_{cj} as j becomes large. In brief, the results of our simulations are, first, that the wetting transition does indeed appear and has qualitatively the same properties as found from the mean-field calculation and, second, that T_{cj} at large j appears to approach a constant value $T_{c\infty}$ well below T_3 and only slightly above T_2 in agreement with the expectation expressed by de Oliveira and Griffiths. It seems likely that $T_{c\infty}$ is the same as the roughening temperature T_R. The remainder of this paper is organized as follows: The lattice gas model is presented in Sec. II along with a description of the procedures used in performing the simulations, while Sec. III contains the results and a discussion.

II. MODEL AND NUMERICAL PROCEDURES

Our lattice gas is equivalent to that used in Refs. 1 and 2. The particles of the gas are allowed to occupy the atomic sites of a face-centered-cubic (fcc) structure whose c axis is normal to the surface of the substrate. Any site may be occupied by at most one particle. The substrate is approximated as a continuous distribution of particles occupying the half-space $z<0$; the coordinate z axis is parallel to a $\langle 111\rangle$ direction of the fcc structure. The interparticle interactions are taken here to be nearest-neighbor only as in Ref. 1 and in some of the work described in Ref. 2. The corresponding Hamiltonian is

$$H_g = -\epsilon \sum_{\langle ni,n'i'\rangle} \sigma_{ni}\sigma_{n'i'} , \tag{1}$$

where σ_{ni} is 0 or 1 according to whether the site (ni) is empty or occupied, and the sum is over all nearest-neighbor pairs of atomic sites. The nearest-neighbor interaction energy $-\epsilon\,(\epsilon>0)$ is negative. The indices (ni) are such that $n=1,2,\ldots$ specifies a layer at fixed z or distance from the substrate and i locates a site within that layer; the $n=1$ layer is closest to the substrate.

There is also an external potential, arising from the substrate, acting on each particle of the lattice gas. This approximation of a smooth potential is invariant under translations in the x and y directions and so provides an external Hamiltonian of the form

$$H_e = \sum_{ni} V_n \sigma_{ni} , \tag{2}$$

V_n is the interaction energy of a particle in the nth layer with the substrate. Two different sets of V_n's have been used in the simulations reported here. The first of these, which we shall call potential A, is

$$V_1 = -7.85\epsilon , \quad V_n = -4.2\epsilon/n^3 , \quad n>1 . \tag{3}$$

This is the substrate potential used by de Oliveira and Griffiths; when we employ it our model is identical to theirs in the mean-field approximation. The second substrate potential that we use, potential B, is one that was employed in Ref. 2; specifically, it is

$$V_n = 1.058\epsilon\left(\frac{1}{(0.027+0.973n)^9} - \frac{3}{(0.027+0.973n)^3}\right) . \tag{4}$$

This is the potential specified by Eq. (4) of Ref. 2 when $\alpha=0.85$. Given this external potential our model is identical to the one which gives in the mean-field approximation the phase diagram shown in Fig. 5 of Ref. 2.

Our reason for using these two different substrate potentials is that potential A is so attractive as to produce complete wetting at all T; we may examine the T_{cj} in this case without the added complication of a wetting transition. Potential B, on the other hand, is sufficiently weakly attractive to give a wetting transition at a convenient temperature. In addition both potentials have the virtue that the results of the simulations may be conveniently compared with extant published mean-field calculations.

It is useful to transform the Hamiltonian by introducing $S_{ni}=2\sigma_{ni}-1$. Then $S_{ni}\equiv\pm1$ and, aside from an additive constant,

$$H = H_g + H_e = -\frac{\epsilon}{4}\sum_{\langle ni,n'i'\rangle} S_{ni}S_{n'i'} + \sum_{ni}\left(\frac{V_n - Z\epsilon}{2}\right) S_{ni} , \tag{5}$$

where $Z=12$ is the coordination number of the fcc structure. The grand partition function of the system is, aside from a trivial multiplicative factor,

$$Z = \sum_{\{S\}} \exp\left\{ -\beta\left[-\frac{\epsilon}{4}\sum_{\langle ni n'i'\rangle} S_{ni}S_{n'i'} + \sum_{ni}\left(\frac{V_n-\mu'}{2}\right)S_{ni}\right]\right\} , \tag{6}$$

where the brackets $\{\cdots\}$ denote a sum over all possible sets of S_{ni}'s and $\mu'\equiv\mu+Z\epsilon$ is equivalent to the chemical potential; μ' is such that when $T<T_3$, the dense phase of the bulk lattice gas is stable for $\mu'>0$ and the dilute phase is stable for $\mu'<0$.

This grand partition function is formally identical to the partition function of an Ising model whose spins are in a nonuniform external field given by $(\mu'-V_n)/2$ at site (ni). We have chosen to simulate the Ising model, which is a canonical ensemble problem, and interpret our results in the context of the lattice-gas model. We use the standard Monte Carlo method of Metropolis *et al.*[11] Periodic boundary conditions are employed in directions parallel to the plane of the substrate surface. In most simulations the size of the lattice in these directions was 30 × 30; sometimes 40 × 40 was also used to check the size dependence of critical temperatures. Lattices of considerably lesser size were occasionally explored; these exceptional cases will be noted in the discussion of Sec. III. In the z direction, the substrate provides the necessary boundary condition at the bottom of the lattice. At the top we used one of two devices to close the system. The first was to put a second substrate identical to the first above the top layer of the lattice which was given a sufficient number of layers (anywhere from twelve to thirty) that there were a half-dozen or more layers of uniform dilute gas between the two adsorbed films. The other procedure used to close the system was to apply to the top layer of the lattice an external potential equal to the average interaction energy that a particle in this layer would have with a bulk equilibrium dilute gas lying above. The number of active layers used with this boundary condition varied between six and fifteen. For the simulation of very thick films, the same stratagem was used to discard the first few layers of the lattice. In this case, these layers were essentially filled and their effect on higher layers is faithfully represented by an appropriate mean field.

For a given chemical potential and temperature, we first made runs of some 600 passes through the lattice, attempting to flip each spin once on the average in each pass. The spins were picked either at random or sequentially and the random number generator seeds were usually, but not always, scrambled after each pass. Results using different combinations of these procedures were compared and no discrepancies found. Runs were made using at least two starting configurations[12] at each μ and T. The coverage in each layer and the energy were computed and stored after each pass. At the completion of each run, these quantities and their fluctuations were averaged backwards from the final configuration and the results for the final 30, 60, 90, etc., passes printed as well as the averages from each set of 30 passes. By studying these averages we could usually determine easily whether and when equilibrium had been achieved. If it had, we also could determine, in particular, the coverage θ defined as

$$\theta = \sum_n (\langle \sigma_n \rangle - \langle \sigma_\infty \rangle) \ ,$$

where $\langle \sigma_n \rangle$ is the probability in equilibrium that a site in layer n is occupied and $\langle \sigma_\infty \rangle$ is the probability that a site far from the substrate is occupied.

For many sets of parameters μ, T not too close to a critical point these relatively short runs proved sufficient to determine the equilibrium thermodynamic properties with acceptable accuracy. When they were not sufficient, runs of 2000, 4000, 6000, or in a few special cases, 20 000 passes through the lattice were performed. The averaging procedures used in each case were the same as described above except that results from groups of 100, 200, 300, or 1000 passes were averaged and printed.

III. RESULTS AND DISCUSSION

We shall discuss separately the work using each of the substrate potentials.

Potential A

This potential, given by Eq. (3), is such that there is complete wetting at all temperatures. The interesting feature of the film's phase diagram is the existence of an apparently infinite number of first-order phase transitions in which the coverage θ changes by an amount of order one corresponding to the addition of a single layer of particles to the absorbed film. In the mean-field approximation, the critical temperatures T_{cj} of these transitions appear to approach the bulk three-dimensional critical temperature as j becomes large.[13] In Fig. 1 we show as a histogram the critical temperatures T_{cj} found for the first nine phase transitions. Qualitatively, this figure resembles the T-θ phase diagram which we did not show because the rather coarse temperature mesh used does not allow us to determine with any accuracy the shapes of the two-phase coexistence curves in the vicinity of each T_{cj}. It would be misleading, therefore, to present such a phase diagram. From the figure, one sees that the critical temperature of the first layer, T_{c1}, is very close to that of the triangular net of $0.911\ \epsilon/k$; T_{cj} rises with j, approaching a value close to $1.025\epsilon k$. We have examined T_{cj}'s for $j \leq 14$ and this limiting value appears to be well established. The critical temperatures were found by executing runs at in-

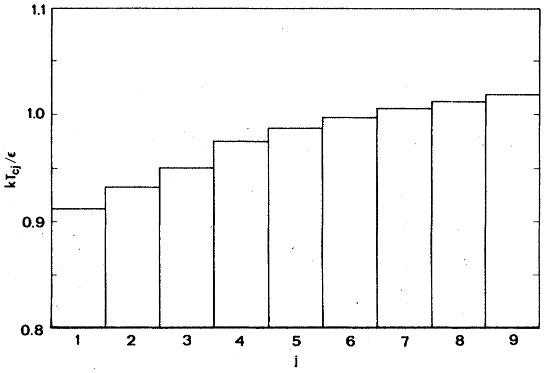

FIG. 1. The critical temperatures T_{cj} using substrate potential A. The histogram is simply the T-θ phase diagram with the phase equilibrium curves represented by rectangles.

tervals of $0.025\epsilon/k$ in temperature around each T_{cj} using lattices measuring both 30×30 and 40×40 in constant z planes. These were done as nearly as possible at the critical value of μ', μ'_{cj}, which was found from some preliminary runs slightly below T_{cj}. In general, μ'_{cj} is just a bit more negative than V_j [see Eq. (3)] and was easy to locate to within $0.001\epsilon/k$ for j beyond about 3. The following procedures were used in order to determine T_{cj}: 600-pass runs were initiated at coverages of $j-1$ and j layers. If in both cases the coverage did not change appreciable, i.e., by an amount of order one layer, for the full 600 passes then it was deemed that $T<T_{cj}$ and there are two distinct phases in equilibrium. If the coverage changed from $j-1$ to j and/or j to $j-1$ (roughly speaking), then longer runs were executed and particular attention paid to both the number of passes on the average that the system remained around j or $j-1$ layer of absorbate and also the number of passes required for it to cross between these coverages. In addition, the distribution of coverages was examined as well as fluctuations in the coverage of each layer. No single quantitative criterion was used to decide whether T was above or below T_{cj}. Roughly speaking, if θ showed small fluctuations around j or $j-1$ layers for some hundreds of passes and crossed from one coverage to the other fairly quickly—in a hundred passes or so—T was considered to be below T_{cj}. If, on the other hand, large fluctuations in the coverage of the jth layer occurred more or less continually with a rather slow drift of the coverage of this layer between mostly empty and mostly filled, then T was presumed to be at or somewhat above T_{cj}. When apparently contradictory conclusions could be drawn from different runs, additional ones were performed. We believe the critical temperatures to be accurate to $\pm 0.025\epsilon/k$ within the context of a system whose extent is 40×40 in each layer. The difference between the T_{cj}'s given by the two lattices of different size is generally less than the uncertainty, $0.025\epsilon/k$, in the critical temperature. As a check on our method of identifying the T_{cj}'s we simulated a single layer in the absence of an external field, i.e., the Ising model on a triangular net; the critical temperature of this system is $T_c=0.911\epsilon/k$. Using a 30×30 net we find $0.95\epsilon/k$ to be clearly above T_c and $0.90\epsilon/k$ to be clearly below while $0.925\epsilon/k$ was judged to be slightly below. For the 40×40 net, on the other hand, $0.925\epsilon/k$ was judged slightly above, the conclusions for the other temperatures being the same as for the 30×30 net. Consequently, we feel it is reasonable to estimate the error in the T_{cj}'s of Fig. 1 at $0.025\epsilon/k$ and to say that they are, if anything, probably too high as a consequence of the finite size of the system.

The limiting value of T_{cj} for large j, $T_{c\infty}$, is probably closely related to the roughening transition for a $\{111\}$ surface of the fcc lattice gas[1]; It is certainly tempting to speculate that $T_{c\infty}$ is identical to T_R. We tried to investigate this point further by also performing simulations using a simple cubic lattice with a $\langle 100\rangle$ direction normal to the substrate. For this structure, our conclusion from simulations using a lattice measuring 40×40 in planes parallel to the substrate is that $0.600>kT_{c\infty}/\epsilon>0.575$. Simulations on a square net give clearly $0.600\epsilon/k>T_c$, $0.550\epsilon/k<T_c$, and $0.575\epsilon/k$ can be judged neither above nor below T_c; we would be inclined to identify the latter number as T_c. In fact, $T_c=0.567$ for the square net.[14] Hence we feel that our accuracy in this instance is at least as good as for the hcp structure.

There exists a number of other simulations designed to locate the roughening temperature of a simple cubic structure. Leamy and Gilmer[15] started from a lattice gas or isotropic Ising model such as ours but placed constraints on the possible configurations in such a way as to wind up treating the solid-on-solid, or SOS, model for which they found $T_R=0.64\epsilon/k$. Perhaps the best simulation of this model is that of Swendsen[16] who finds $T_R=0.575\pm 0.025$. We are unfortunately unaware of any simulations of roughening in the isotropic Ising model with which our $T_{c\infty}$ may be compared. The most we can say is that $T_{c\infty}$ appears to be about what one would expect for T_R.

POTENTIAL B

The second substrate potential, Eq. (4), is sufficiently less attractive than the first that the mean-field approximation predicts[2] no wetting for $kT/\epsilon<1.35$, partial wetting for $1.35<kT/\epsilon<2.46$, and complete wetting for $2.46<kT/\epsilon$. For this potential we performed simulations at numerous values of μ' and at temperature steps of $0.1\epsilon/k$; near the critical temperature T_{cf} for the partial-wetting to complete-wetting transition the temperature steps were $0.025\epsilon/k$. In these simulations it proved to be very easy to establish the existence of the phase transition but difficult to determine accurately the coexistence curve for the two adsorbed phases. The reason for this difficulty is that at temperatures appreciably below T_{cf}, the two phases are sufficiently different in character—one consisting of a partial adsorbed layer only and the other of several or more layers—and thermal emergies are sufficiently small that many thousands of passes through the lattice are required to observe a transition from one phase to the other. Because our technique for deciding

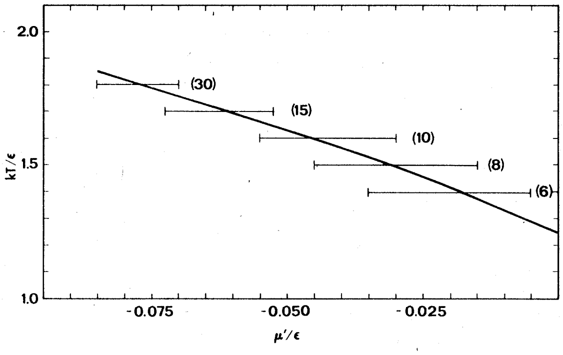

FIG. 2. The T-μ' phase diagram using substrate potential B. The numbers in parentheses specify the size in the x-y plane of the system used in the simulations.

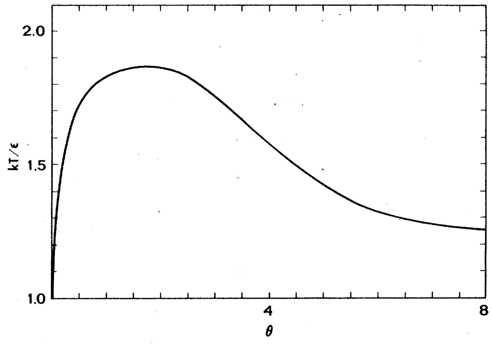

FIG. 3. The T-θ phase diagram using substrate potential B for equilibrium chemical potentials from the curve in Fig. 2.

when the two phases are in equilibrium requires observing this transition and being able to judge in which of the two phases the system prefers to spend most of its time, we are not able to determine accurately the chemical potential at which the phases coexist in equilibrium and hence the phase coexistence curve. Further, as T decreases, we have to use lattices of increasingly restricted size in planes parallel to the substrate surface in order to see the phase transitions at all, and our results probably differ significantly from what would be obtained for an infinite system.

In Fig. 2 we present the T-μ' phase diagram for partial wetting including error bars showing the uncertainty in the equilibrium value of μ'. In parentheses are given the sizes in the x-y plane of the lattices used. Figure 3, which may be compared with Fig. 5 of Ref. 2, is the T-θ phase diagram assuming phase equilibrium occurs at those values of μ' specified by the curve in Fig. 2. According to the latter figure, the two phases are in equilibrium at $T = 1.25\epsilon/k$ for $\mu' = 0$; this is thus the temperature T_{AL} of the no-wetting to partial-wetting transition. In view of the uncertainties in the equilibrium value of μ', this temperature must be regarded as very approximate. It does, however, seem clear that T_{AL} is significantly higher than T_R. There seems to be no reason why T_{AL} should in general bear any particular relation to T_R since the onset of wetting appears when the free energies of a film of essentially infinite thickness and of a partial adsorbed layer become equal; the roughening transition is accompanied by a lowering in the free energy of the thick film but is unrelated to the properties of the adsorbed partial layer. Hence we may expect that the presence of roughening will result in a somewhat lower value of T_{AL} than would be found in the absence of roughening, but that it will not otherwise affect the wetting transition. The critical temperature for the partial-wetting to complete-wetting transition is $1.85 \pm 0.05\epsilon/k$ according to the simulations using a 40×40 lattice; this value is, as expected, significantly lower than that found in the mean-field approximation, or $2.46\epsilon/k$.

In summary we find that Monte Carlo simulations of the lattice-gas model of adsorption verify the existence of the wetting transition in this model and also give strong evidence of the existence of a roughening transition in the interface between the condensed and gaseous phases of the system at a temperature not much higher than the two-dimensional critical temperature of a single layer of the lattice gas.

ACKNOWLEDGMENTS

The author wishes to thank Professor Michael Wortis and Professor W. F. Saam for useful conversations concerning the wetting and roughening transitions. He is indebted to Dr. D.-Y. Kuan for assistance with the early stages of the work. This research was supported in part by a grant from the National Science Foundation.

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[12] For example, films of N and $N+1$ filled layers or 0 and N layers, where N is any integer from 1 to 15, the remainder of the lattice being empty.

[13] See Figs. 2 and 3 of Ref. 1 and related discussion.

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