Phase diagrams of multilayer films and the Potts lattice-gas model of adsorption

C. Ebner

Department of Physics, The Ohio State University, Columbus, Ohio 43210
(Received 18 March 1983)

The Potts lattice-gas model is examined via Monte Carlo simulations and a mean-field approximation to obtain phase diagrams for multilayer adsorbed films. The advantage of the model is that it has three bulk phases, interpreted here as solid, liquid, and gas, allowing one to study the relationships between the phase transitions of the film and the bulk triple point. For our choices of coupling parameters, we find a solid film that wets the substrate and that melts, forming a liquid film, below the bulk triple-point temperature and either above or below the bulk roughening temperature. The liquid film wets the substrate above the bulk triple point but not below.

The phases and phase transitions of multilayer adsorbed films are of considerable current theoretical[1-5] and experimental[6-8] interest. Because of the complexity of the physical systems involved, theorists have frequently made recourse to simple lattice models in order to obtain specific detailed predictions of the films properties. The model primarily used has been the Ising lattice gas[3,9,10] in which each lattice site has just two states, occupied or empty. This model has the shortcoming that below its critical temperature it has only two bulk phases, a dilute one which is interpreted as a gas and a dense one which may be interpreted as liquid or solid, depending on the application. In this paper, we employ a Potts lattice-gas model which has a more realistic bulk phase diagram in that there are two dense phases as well as a dilute one, with all three phases meeting at a triple point. With this model, we examine multilayer adsorption, looking in particular at melting and wetting transitions and their relationship to the bulk triple point.

For the sets of coupling parameters reported here, and using mean-field calculations and Monte Carlo simulation, we find the following general behavior of the adsorbed film: at low enough temperature T, there is a solid film which completely wets the substrate. There are first-order layering transitions in this film which, as T rises, may or may not end at critical points before the film melts, depending on the choice of coupling parameters. The melting temperature lies below the bulk triple point temperature T_3. The liquid film which forms upon melting does not wet the substrate for $T < T_3$. Thus we find that the melting transition is accompanied by a transition from wetting (in the solid phase) to nonwetting (in the liquid phase) as T increases. For $T > T_3$, the liquid film does wet the substrate. All of these features are present in both the Monte Carlo and the mean-field work with the exception of the ending of the layering transitions at critical points before the film melts. This feature appears only in the simulations; the mean-field approximation in general grossly overestimates the temperatures of the critical points,[9,10] placing them above the melting temperature of the film in those cases reported here.

We turn now to a detailed description of the model. The lattice is an fcc structure with a $\langle 111 \rangle$ direction normal to the substrate. The Hamiltonian may be written as

$$H = - \sum_{\langle ni\alpha; n'i'\alpha' \rangle} J_{\alpha\alpha'} t_{ni\alpha} t_{n'i'\alpha'} - \sum_{ni\alpha} V_{n\alpha} t_{ni\alpha} \ . \tag{1}$$

The first sum is over all pairs of nearest-neighbor sites ni and $n'i'$. The index i identifies a site within a layer n of the lattice, each layer being at a fixed distance from the substrate. The indices α and α' run from 1 to $q+1$; $\alpha = 1$ represents an empty site while for the remaining q states (the Potts states), there is a particle at the site. The occupation number $t_{ni\alpha}$ is one if state α is occupied at site ni, otherwise it is zero. In a given state of the system and for a given site, one of the $t_{ni\alpha}$ is unity and the rest are zero. The coupling constants $J_{\alpha\alpha'}$ are $J_{\alpha 1} = J_{1\alpha} = 0$ for all α; $J_{\alpha\alpha} = J$, $\alpha > 1$; and $J_{\alpha\alpha'} = \gamma J$, $\alpha \neq \alpha'$ and $\alpha, \alpha' > 1$. The energies J and γJ are positive to represent an attractive interaction between particles; γ is less than 1 so that the binding energy is larger when the same Potts state is occupied on neighboring sites than when different states are occupied. The parameters $V_{n\alpha}$ represent the interaction of a particle with the substrate; in the work reported here we have used $V_{n1} = 0$, $V_{1\alpha} = 7.85J$, and $V_{n\alpha} = 4.2J/n^3$, $n > 1$, parameters appropriate for Kr on graphite.[11] These values give a "strong" substrate potential in that it leads to complete wetting at all temperatures when used with the Ising lattice-gas model.[9,10]

The bulk phases of this model are a "gas" in which most sites are empty, a "liquid" in which most sites are occupied but no one Potts state is preferred, and a "solid" with most sites occupied and one preferred Potts state. The liquid-solid transition is first order if q is sufficiently large. We want this transition to be strongly first order in three dimensions to imitate simple real systems such as the rare gases as well as possible; to this end we have chosen $q = 6$ in the present work. As for the parameter γ, we have used two values, 0.5 and 0.633; the reasons for these choices will become clear from the discussion below.

The bulk and film phase diagrams for the model have been examined using both a mean-field approximation and Monte Carlo simulations. The procedures followed parallel closely those described in Refs. 9 and 10 with one exception; the Monte Carlo work has been extended by computing the energy and number densities ϵ and n along various paths in the space of chemical potential μ and T and then doing appropriate integrals to obtain the grand free energy ω, thus allowing for more accurate determination of the location of first-order phase boundaries. For the bulk simulations, lattices range in size from $6 \times 6 \times 6$ to $10 \times 10 \times 10$ with

typically 1400 passes through the lattice. To obtain the film phase diagrams, we employed lattices as large as $40 \times 40 \times 12$ with two to three thousand passes. Systems with lateral dimensions as small as 20×20 were used with fewer passes at points (μ, T) where fluctuations were small, i.e., far from critical regions and weakly first-order transitions. The resulting uncertainty in the first-order phase boundaries is quite small, probably no larger than the widths of the lines in the figures. The uncertainties in the critical temperatures are around $\pm 0.02 kT/J$ as a consequence of finite-size effects.

In Fig. 1 we show the (Monte Carlo) bulk and film phase diagrams in the $\mu - T$ plane for $\gamma = 0.633$; this value of γ is such that T_3/T_c, where T_3 and T_c are the bulk triple point and critical temperatures, is about the same as for the rare gases. The zero of chemical potential is chosen to be such that for $\mu = 0$, the bulk gas and solid phases are in equilibrium at $T = 0$; that is, the quantity which enters the grand partition function is $H - (\mu - 6J)N$ where N is the number of occupied sites (sites with $\alpha > 1$). The bulk phase diagram has appropriate qualitative features; perhaps its most serious shortcoming is that the liquid-solid phase boundary is nearly vertical as a consequence of the model giving short shrift to effects arising from the repulsive cores of real atoms.
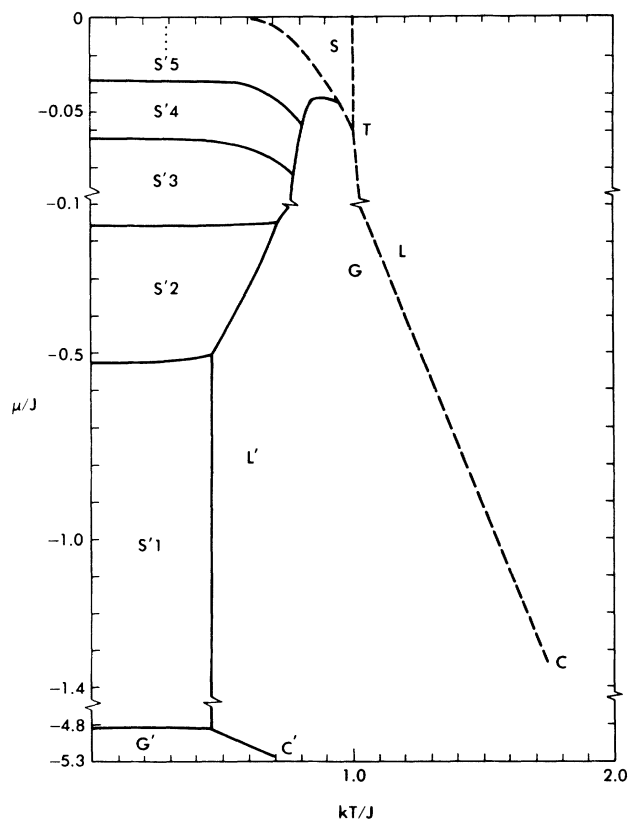
As for the film, we see from the figure that there are

fluid and solid phases with layering transitions in the solid. The first layer of liquid is separated from the gas via a first-order transition which ends in a critical point. The layering transitions in the solid do not end at critical points but rather at the melting line. As one moves upward along this line, he finds that the liquid film grows continuously in thickness reaching, at the saturated vapor pressure, a finite thickness. In contrast, the solid film completely wets the substrate at all temperatures. We have, then, a transition from wetting to nonwetting as T rises; the transition is accompanied by the solid-liquid transition which has not heretofore been included in calculations of wetting phenomena.

On the saturated vapor pressure (bulk gas-solid) line for $T < T_3$ but T larger than the melting temperature of the film, the liquid film has a finite thickness which increases at T_3 is approached, apparently going continuously to bulk liquid at the bulk triple point. One may understand this behavior by considering the extension of the bulk liquid-vapor line into the region of bulk solid[12] where it separates metastable bulk liquid and vapor phases. With this picture, we see that in moving along the bulk solid-vapor line, we are simply approaching the liquid-vapor line at an angle and that the liquid film is growing continuously to form bulk liquid when we reach this line, i.e., at the triple point, in the usual way for a liquid film that completely wets the substrate. We are prevented from seeing this behavior at $T < T_3$ because it is preempted by the formation of the bulk solid.

Figure 2 displays the (Monte Carlo) film phase diagram for $\gamma = 0.5$. By using this smaller value, we effectively

FIG. 1. Bulk and film phases for $\gamma = 0.633$. The bulk gas, liquid, and solid phases are denoted G, L, S, respectively. They are separated by dashed ($- - -$) lines with triple point T and critical point C. The corresponding film phases are G', L', and $S'n$ where n denotes the number of molecular layers in the film. These phases are separated by solid lines all of which represent first-order transitions.
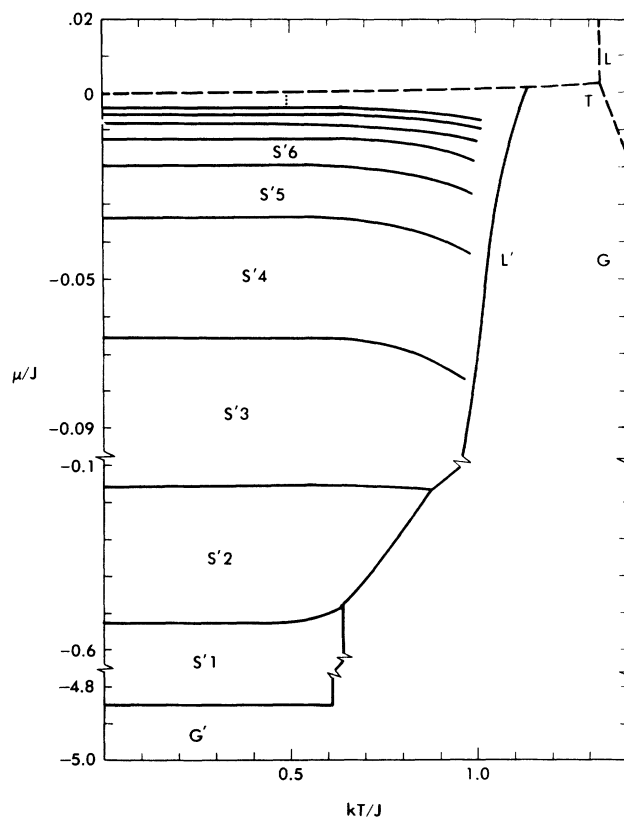

FIG. 2. Bulk and film phases for $\gamma = 0.500$. The notation is the same as in Fig. 1.

reduce the stability of the liquid relative to the solid and so move the melting lines to higher temperatures. This resulting phase diagram differs qualitatively from the preceding one in the following two respects: there is no longer a first-order line separating the gas from a single layer of adsorbed liquid. This transition is preempted by the formation of the solid film. In the same way, the melting transition in the multilayer region has moved to sufficiently high temperatures that the transition for adding layers beyond the third to the solid film now end at critical points with critical temperatures T_{cn} that increase slowly with n, the numbers of layers. For $n = 10$, $kT_{c10}/J \simeq 1.02$. We expect that T_{cn} does not change much more as $n \rightarrow \infty$ and that it approaches the roughening temperature of a [111] face of the model.[9,10] This case thus has the property that the solid film may grow either by discrete steps or continuously, depending on the temperature. Such behavior has been observed in a number of systems.[8]

There do not appear to be complete measurements of the thick-film phase diagram of any simple system with which the phase diagrams generated here may be compared. Certainly it would be useful to have such measurements. One should bear in mind, however, that our results are limited in that only one substrate potential has been considered.

Changes in the relative strength of the adatom-adatom and adatom-substrate potentials will produce significant rearrangement of the wetting transitions in particular. Also, one may suppress the melting lines by increasing γ and thereby expose first-order transitions in which the liquid film thickness increases by jumps of about one molecular layer. Indeed, for $\gamma = 0.633$ we were able to locate the critical point for the transition from one layer to two in the region of metastable fluid close to $kT/J = 0.7$ and $\mu/J = -0.17$. We are currently embarking on a more thorough investigation of the possible behavior of the model.

In summary, we have used the Potts lattice-gas model to study the physical adsorption of multilayer films. The model is superior to the Ising lattice gas in that it has two dense phases, interpreted as liquid and solid, in addition to a dilute one. Thus one may study unambiguously both liquid and solid films under a vapor and may look at the relationship of the layering, roughening, wetting, and melting transitions in the film to the various phase transitions, including the triple point, in the bulk as well as to each other.

---

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

[2]C. Ebner and W. F. Saam, Phys. Rev. Lett. 38, 1486 (1977); J. W. Cahn, J. Chem. Phys. 66, 3667 (1977).

[3]R. Pandit and M. Wortis, Phys. Rev. B 25, 3226 (1982).

[4]R. Pandit, M. Schick, and M. Wortis, Phys. Rev. B 26, 5112 (1982).

[5]W. F. Saam, Surf. Sci. (in press); C. Ebner, C. Rottman, and M. Wortis, Phys. Rev. B (in press).

[6]S. Ramesh and J. D. Maynard, Phys. Rev. Lett. 49, 47 (1982).

[7]M. R. Moldover and J. W. Cahn, Science 207, 1073 (1980); O' D. Kwan, D. Beaglehole, W. W. Webb, B. Widom, J. W. Schmidt, J. W. Cahn, M. R. Moldover, and B. Stevenson, Phys. Rev. Lett.

48, 185 (1982); D. W. Pohl and W. I. Goldberg, ibid. 48, 1111 (1982).

[8]Y. Larher, Mol. Phys. 38, 789 (1979); Y. Larher and F. Millot, J. Phys. (Paris) Colloq. 38, C4-189 (1977), and references contained therein.

[9]M. J. de Oliveira and R. B. Griffiths, Surf. Sci. 71, 687 (1978); C. Ebner, Phys. Rev. A 22, 2776 (1980).

[10]C. Ebner, Phys. Rev. A 23, 1925 (1981).

[11]W. A. Steele, The Interaction of Gases with Solid Surfaces (Pergamon, Oxford, 1974).

[12]I am indebted to Professor M. Schick for the correct interpretation of this feature of the phase diagram.