

## Monte Carlo study of phase transitions in a confined lattice gas

D. Nicolaides and R. Evans

*H. H. Wills Physics Laboratory, University of Bristol, Bristol BS8 1TL, United Kingdom*

(Received 4 August 1988)

The phase diagram of a lattice gas confined between two parallel adsorbing walls is investigated via Monte Carlo simulation. For large wall separations, we find a line of first-order capillary-condensation transitions at chemical potentials shifted to smaller values,  $\mu(T)$ , than the bulk value  $\mu_{\text{sat}}(T)$ . We also find a line of first-order prewetting transitions, terminating in a prewetting critical point and intersecting the line of capillary-condensation transitions in a triple point where thin-film, thick-film, and "liquid" phases all coexist. Although such a rich phase diagram had been conjectured earlier on the basis of mean-field calculations and thermodynamic arguments, we believe this is the first confirmation by simulation.

### I. INTRODUCTION

The influence of confinement of a fluid on its bulk and surface phase transitions is a subject of considerable recent interest.<sup>1</sup> The phase diagram of a fluid confined in slitlike geometry is predicted by mean-field treatments of lattice models<sup>2</sup> and by density-functional theories of continuum fluids<sup>1,3</sup> to be extremely rich and a complete exploration of this by Monte Carlo simulation is not feasible. However, one of the main features of confinement—that of bringing the bulk liquid-gas phase transition into competition with those surface phase transitions occurring for an undersaturated bulk—is evident in a restricted region of the full phase diagram, which we have explored in detail by simulation. Specifically, consider a fluid in contact with a reservoir at constant chemical potential  $\mu$  and temperature  $T$ , and confined between two identical parallel adsorbing walls separated by a finite distance  $H$  in the  $z$  direction, but of infinite area in the  $x$  and  $y$  directions. Interactions between the walls and the fluid are represented by an external potential which varies only with  $z$  (perpendicular to the walls). Then, if the attractive part of the wall potential is of "moderate" strength so that a first-order wetting transition, with its accompanying prewetting or thick- to thin-film transition,<sup>4,5</sup> occurs for a single wall ( $H = \infty$ ) the mean-field analysis of Refs. 2 and 3 suggests that the phase diagram is of the form depicted in Fig. 1(a). The genesis of such a diagram is best understood by reference to the  $(T, \mu)$  phase diagram for lattice-gas adsorption at a single wall—see Fig. 1(b). In this case, the prewetting line  $AB$  extends from the point of the wetting transition  $(T_w, \mu_{\text{sat}})$  to the prewetting critical point  $(T_{\text{pwc}}, \mu_{\text{pwc}})$  where the distinction between thick and thin adsorbed films disappears. Note that  $T_w < T_{\text{pwc}} < T_c$  and  $T_c$  is the bulk critical temperature. For  $T_w < T < T_{\text{pwc}}$  thin adsorbed films are stable for  $\mu < \mu_{\text{pw}}$  while thick films are stable for  $\mu > \mu_{\text{pw}}$ . These coexist on the prewetting line  $\mu = \mu_{\text{pw}}(T; H = \infty)$ . When the lattice gas is confined, so

that  $H$  is finite, the bulk coexistence curve is shifted to  $\mu < \mu_{\text{sat}}$  by an amount that is proportional to  $1/H$  for sufficiently large  $H$ . Such a shift is termed capillary condensation.<sup>1,2</sup> If  $H$  is large enough prewetting can still occur at both walls before condensation of the dense "liquid" filling the capillary takes place. (In contrast to the wetting transition, prewetting is a surface transition occurring out of bulk coexistence so it does not require infinite  $H$ .) Mean-field calculations<sup>2,3</sup> and general thermodynamic arguments<sup>6</sup> indicate that prewetting is very weakly dependent on  $H$ , i.e.,  $\mu_{\text{pw}}(T; H) \approx \mu_{\text{pw}}(T; \infty)$ . One then expects that for some  $\mu_{\text{pw}} < \mu < \mu_{\text{sat}}$  capillary condensation to "liquid" should occur. It is evident from Fig. 1(b) that for sufficiently large  $H$  a triple point is expected where "thin," "thick," and "liquid" states will coexist. For small wall separations  $H$  capillary condensation will occur at some  $\mu < \mu_{\text{pwc}}$  and prewetting will not occur as a transition between stable states. Then the surface  $ABC$  of prewetting transitions in Fig. 1(a) will be occluded by the surface of condensation transitions.

It is the aim of the present work to investigate the competition between capillary condensation and the prewetting surface phase transition thereby testing the predictions of the mean-field treatments. There are three main reasons we chose to perform simulations for a lattice-gas model, rather than a continuum fluid. (i) Lattice models are generally much better suited to very large scale Monte Carlo simulation. This is important for the present problem where mean-field calculations indicate very large wall separations are required if prewetting between stable states is to take place. (ii) We could draw on work of Sen and Ebner<sup>7</sup> who had performed simulations of prewetting for a lattice gas near a single wall. (iii) Prewetting had not been observed in *any* simulations of continuum models.<sup>8</sup> Our paper is arranged as follows. In Sec. II we describe the lattice model and the details of the computations. The results of the simulations are presented in Sec. III. We conclude in Sec. IV with a discussion of our results and make some comparisons with the earlier mean-field treatments.

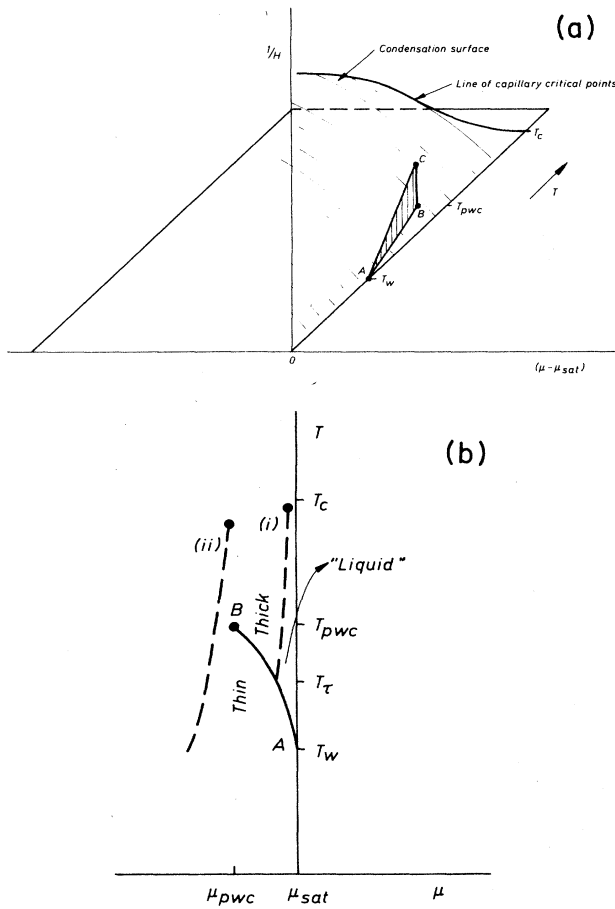


FIG. 1. (a) Schematic phase diagram of a confined lattice gas in the prewetting region, as a function of the wall separation  $H$ , temperature  $T$ , and chemical potential  $\mu$ . The surface of capillary-condensation transitions is bounded on its right by the bulk coexistence line, and on its left by the line of capillary critical points. The prewetting surface  $ABC$  is bounded by the prewetting line  $AB$  in the  $1/H=0$  plane, a line of prewetting critical points  $BC$ , and a line of triple points  $AC$  where it intersects the condensation surface. (b) A schematic  $(T, \mu)$  phase diagram for a lattice gas. Bulk coexistence occurs at  $\mu = \mu_{\text{sat}}$ .  $AB$  denotes the prewetting line with  $H = \infty$ . On confining the system at large  $H$  the prewetting line is hardly altered but capillary condensation occurs at  $\mu < \mu_{\text{sat}}$  [dashed curve (i)]. For  $T_\tau < T < T_{\text{pwc}}$  phase transitions from "thin" to "thick" to "liquid" occur as  $\mu$  is increased.  $T_\tau$  is the triple-point temperature for this separation  $H$ . When  $H$  is small prewetting is precluded by capillary condensation at  $\mu < \mu_{\text{pwc}}$  [dashed curve (ii)]. Note that each condensation line ends in a critical point corresponding to a shifted bulk critical point.

## II. THE MODEL AND COMPUTATIONAL DETAILS

The Hamiltonian of our lattice-gas model is

$$H = -\epsilon \sum_{\langle jK, j'K' \rangle} \sigma_{jK} \sigma_{j'K'} + \sum_{j=1}^M V_j \sum_K \sigma_{jK}. \quad (1)$$

Here  $\epsilon$  (positive) is the interparticle potential between nearest neighbors and the sum in the first term is over all

nearest-neighbors pairs of sites:  $\sigma_{jK}$  is 1 if site  $K$  in the  $j$ th layer is occupied and is 0 if it is not.  $V_j$  is the total potential affecting a particle in the  $j$ th layer due to the walls. We choose a simple cubic lattice with  $M$  layers in the  $z$  direction and work in the grand canonical ensemble with a given chemical potential  $\mu$ . Bulk liquid-gas coexistence occurs at  $\mu = \mu_{\text{sat}} = -3\epsilon$  and the critical temperature is given by<sup>9</sup>  $k_B T_c / \epsilon = 1.1279$  for the simple cubic structure.

Our choice of wall potential was influenced by work of Sen and Ebner<sup>7</sup> who investigated prewetting in a variety of lattice models. We chose a potential that corresponds closely to one of theirs. Each wall is considered to be composed of atoms on the sites of a semi-infinite simple cubic lattice interacting with fluid atoms via the Lennard-Jones 12-6 potential:

$$\phi_{wa}(r) = R \epsilon \left[ \left( \frac{a}{r} \right)^{12} - 2 \left( \frac{a}{r} \right)^6 \right],$$

where  $a$  is the lattice spacing and  $R$  is a constant. Sen and Ebner found that choosing  $R = 0.31$  gave a first-order wetting transition in a mean-field approximation at  $T_w = 0.5T_c$  and a prewetting line that was rather extensive in temperature:  $T_{\text{pwc}} = 0.81T_c$ . Although they do not consistently calculate  $T_w$  and  $T_{\text{pwc}}$  in their Monte Carlo simulations, they estimate that both temperatures should be lowered below their mean-field values—the prewetting critical temperature more than the wetting transition temperature. Their Monte Carlo results indicate that the prewetting line is shifted closer to bulk coexistence than in a mean field, and they estimate that the critical point is near  $\Delta\mu_{\text{pwc}} \equiv (\mu_{\text{sat}} - \mu_{\text{pwc}}) = 0.030\epsilon$ , whereas the mean-field value is  $0.045\epsilon$ .

We used the same value of  $R$  but approximated the sum over sites in a single wall by the accurate "summed 10-4" formula:<sup>10</sup>

$$V_s(z) = \frac{R \epsilon \pi}{45} \left[ 9 \left( \frac{a}{z} \right)^{10} + \frac{a^9}{(z + 0.72a)^9} - 45 \left( \frac{a}{z} \right)^4 - \frac{15a^3}{(z + 0.61a)^3} \right]. \quad (2)$$

The total wall potential in the confined system is

$$V_j = V_s(ja) + V_s((M+1-j)a). \quad (3)$$

The simulations were performed on the ICL Distributed Array Processor (DAP), and its successor, the Active Memory Technology DAP510. These bit-serial machines are especially well suited to simulation of lattice models. The infinite walls in the  $x$  and  $y$  directions were replaced by a finite area with periodic boundary conditions. The number of sites in a layer,  $L^2$ , was either 1024 or 4096, and we could find no systematic finite-area effects to the level of accuracy of the simulations. The Metropolis spin-flip algorithm was employed, and different numbers of Monte Carlo steps per site were discarded for equilibration or kept for averaging, depending on the state point. For each point on a thermodynamic integration path, 1000 steps were discarded for equilibration and

1000 kept for averaging, while for runs near the prewetting critical point 5000 steps were discarded and 50 000 were kept.

Phase equilibria are best investigated by computing the grand potential  $\Omega$  of the inhomogeneous lattice gas. The state with the lowest value  $\Omega$  is the equilibrium state of the system. Coexistence of two distinct states  $\alpha$  and  $\beta$  occurs when  $\Omega_\alpha = \Omega_\beta$ . A convenient route to the computation of  $\Omega$  can be obtained from the thermodynamic relation<sup>6</sup>

$$d\Omega = -pdV - SdT - Nd\mu + 2\gamma dA - (Af)dH, \quad (4)$$

where  $p$  is the pressure,  $V$  is the volume,  $S$  is the entropy,  $N \equiv \langle \hat{N} \rangle$  is the average number of fluid atoms (occupied sites),  $A$  is the area of one wall, and  $\gamma$  is the wall-fluid interfacial tension (surface-excess grand potential per unit area). The last term in (4) is the work done when the wall separation  $H \equiv Ma$  is increased:  $f$  is the (solvation) force between the two walls. If we work with fixed  $A$  and  $H$  (and hence  $V$ ) we can integrate the Gibbs adsorption equation

$$\left[ \frac{\partial \Omega}{\partial \mu} \right]_T = -N \quad (5a)$$

on an isothermal path and the relation<sup>11</sup>

$$\left[ \frac{\partial(\Omega/T)}{\partial(1/T)} \right]_\mu = U - N\mu \quad (5b)$$

on a path at fixed chemical potential. Here  $U$  is the total internal energy and we have used the definition  $\Omega \equiv U - TS - \mu N$ . The integrations start at sufficiently low  $\mu$  so that the ideal gas result for  $N$  can be employed.<sup>10,11</sup> Thus in the simulation we monitor  $N$  and  $U$  along reversible thermodynamic paths and use (5) to obtain  $\Omega$  for the various phases. In addition we monitor the density (occupancy) profile

$$\rho_j = \frac{1}{L^2} \left\langle \sum_K \sigma_{jK} \right\rangle \quad (6a)$$

and, for purposes of locating the prewetting critical point, the susceptibility

$$\chi \equiv \frac{\langle \hat{N}^2 \rangle}{\langle \hat{N} \rangle^2} - 1, \quad (6b)$$

with

$$\hat{N} = \sum_{jK} \sigma_{jK}.$$

### III. RESULTS OF THE SIMULATIONS

Results of thermodynamic integration of (5), for a slit of  $M=61$  layers, and at a temperature of  $T=0.895T_c$  are shown in fig. 2. This isotherm lies above the prewetting critical temperature  $T_{pwc}$  so there is only one "gas" branch. The error bars indicated were determined by performing thermodynamic integration around reversible closed loops in each phase. The deviation from zero of the resulting grand potential was generally less than 2%

of its value at any single state point. This was of the same size as the asymmetry of the density profiles about the center of the slit, and is probably an overestimate of the true statistical errors in the grand potential.

The grand potentials of "gas" and "liquid" branches are equal when  $\Delta\mu/k_B T_c = 0.00857 \pm 0.00052$ . We can compare this result for capillary condensation with that from the macroscopic Kelvin equation which predicts a shift in the bulk transition by an amount<sup>1,2</sup>

$$\Delta\mu_K = \frac{2(\gamma_{wg} - \gamma_{wl})}{M(\rho_l - \rho_g)}, \quad (7)$$

where  $\gamma_{wg}$  is the (single) wall-gas interfacial tension evaluated at  $\mu = \mu_{sat}$  and  $\gamma_{wl}$  is the corresponding quantity for the wall-liquid interface. These surface tensions are defined as the surface-excess grand potential of the fluid in the slit, i.e.,

$$2\gamma = \lim_{M \rightarrow \infty} \left[ \frac{\Omega}{L^2} + pM \right]$$

and for the lattice model have the dimension of energy.  $\rho_l$  and  $\rho_g$  in (7) are the densities (occupancies) of "liquid" and "gas" at bulk coexistence. Since the "liquid" branch exists at  $\mu = \mu_{sat}$ ,  $\Omega_l$  is well defined at bulk coexistence and  $\gamma_{wl}$  can be estimated by assuming this quantity to be independent of  $M$  for  $M > 61$ .  $\rho_l$  is set equal to the density at the center of the slit. While the "gas" branch extends well beyond the equilibrium transition—see Fig. 2—this metastable portion does not reach  $\mu_{sat}$  in a complete wetting situation.<sup>1,2</sup> Thus it is necessary to extrapolate  $\Omega_g$  to  $\mu_{sat}$  in order to estimate  $\gamma_{wg}$  and this involves some uncertainty. There are similar uncertainties involved in estimating  $\rho_g$ . The resulting Kelvin estimate is  $\Delta\mu_K/k_B T_c \approx 0.0062$ , which is considerably less than the result of the full calculation. Similar discrepancies occur

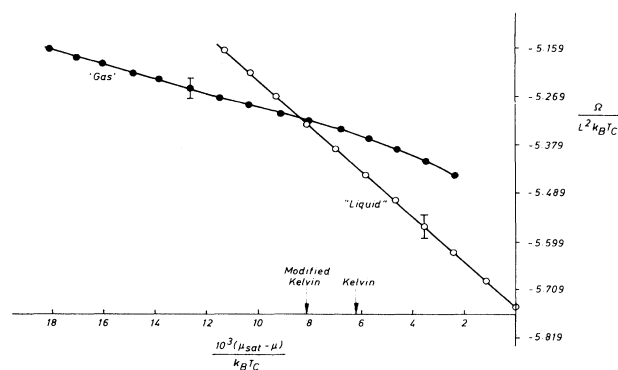


FIG. 2. The thermodynamic grand potential  $\Omega$  as a function of chemical potential, for a system of 61 layers and  $T=0.895T_c$ . The grand potential is measured in units of the bulk critical temperature, and divided by the number of sites in a single layer. Representative error bars are indicated. The two branches cross at  $\Delta\mu = (8.57 \pm 0.052) \times 10^{-3} k_B T_c$ . The arrows locate the predictions of the Kelvin equation [Eq. (7)] and the modified version mentioned in the text.

in mean-field calculations<sup>1,2</sup> when thick wetting films develop at the walls. A modification<sup>12,1</sup> of the Kelvin equation, which takes into account the effects of the films, replaces  $M$  in (7) by  $M - 3ta^{-1}$ , where  $t$  is the thickness of the wetting film, when the walls exert van der Waals forces on the atoms of the fluid. Such a modification was derived first by Derjaguin<sup>13</sup> in 1940. In Fig. 2 we display both the Kelvin and the modified Kelvin estimates. The film thickness, calculated from weighted moments of the density profiles, is  $t = 4.7$  lattice spacings, leading to a substantial correction. The modified Kelvin estimate is  $\Delta\mu_{MK}/k_B T_c \approx 0.0081$ , which is in quite good agreement with the result of the full calculation.

Once the “gas”-“liquid” coexistence curve has been located its slope may be found from the Clapeyron equation<sup>6</sup>

$$\left( \frac{\partial\mu}{\partial T} \right)_{\text{coex}} = \frac{-(U_\alpha - N_\alpha\mu) - (U_\beta - N_\beta\mu)}{T(N_\alpha - N_\beta)} \quad (8)$$

with  $\alpha$  referring to “liquid” and  $\beta$  to “gas.” Equation (8) requires fixed area  $A$  and separation  $M$ . This allows us to follow the phase boundary down to a temperature where it may intersect the prewetting phase boundary. Figure 1(b) indicates that this will occur if the slit is wide enough. We can estimate the minimum separation  $M_{\text{pwc}}$  necessary for prewetting to be observable by an argument<sup>2,3</sup> based on the Kelvin equation. Prewetting between stable phases will occur provided

$$\Delta\mu_{\text{pwc}} > \Delta\mu_K = \frac{2(\gamma_{\text{wg}} - \gamma_{\text{wl}})}{M(\rho_l - \rho_g)}.$$

Thus

$$M_{\text{pwc}} \approx 2(\gamma_{\text{wg}} - \gamma_{\text{wl}}) / (\rho_l - \rho_g) \Delta\mu_{\text{pwc}}.$$

Using the value of  $\Delta\mu_{\text{pwc}}$  given by Sen and Ebner, assuming this does not vary with  $M$ , and using our estimate of the surface tensions and densities, we obtain  $M_{\text{pwc}} \approx 45$ . Thus for slits with  $M \lesssim 45$  we expect any prewetting transition to be between *metastable* films. In theory, a grand canonical Monte Carlo simulation will always give equilibrium results if enough computer time is used but in practice nucleation times can be arbitrarily long and true equilibrium behavior will not be seen.

We performed simulations for just such a situation—a slit with  $M = 31$  layers—and present the results of thermodynamic integrations along the  $T = 0.652T_c$  isotherm in Fig. 3. The transition from a thin adsorbed film to “liquid” (capillary condensation) occurs for  $\Delta\mu/k_B T_c = 0.0352 \pm 0.0004$ , which is quite close to the estimate 0.0314, obtained from Clapeyron equation (8); the latter uses data from the  $T = 0.895T_c$  transition in the same slit. It is clear from Fig. 3 that although there is no stable thick-film configuration in this system, metastable thick films survive and a prewetting transition occurs for  $\Delta\mu_{\text{pw}}/k_B T_c = 0.024 \pm 0.0004$ . Indeed, the metastable films survive for many thousands of time steps. We have even observed the criticality of the prewetting transition between metastable films over times on the order of several-hundred-thousand time steps. The same sort of

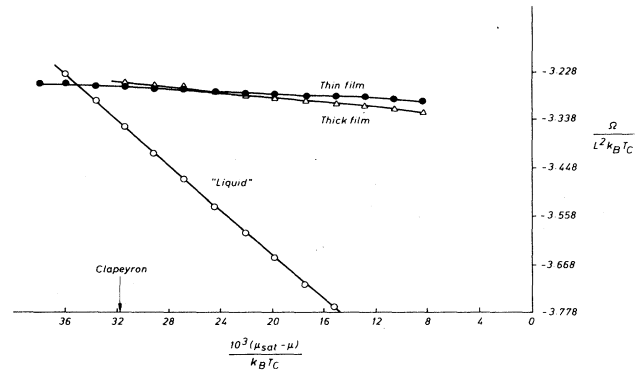


FIG. 3. The reduced thermodynamic grand potential  $\Omega$  as a function of chemical potential for a system of 31 layers and  $T = 0.652T_c$ . The arrow indicates the prediction of the Clapeyron equation [Eq. (8)].

criticality of two metastable states has been utilized recently in simulations of a critical wetting transition.<sup>14</sup>

By increasing the width of the slit to  $M = 61$  layers prewetting should occur between equilibrium states. This is confirmed in Fig. 4. As expected  $\Delta\mu_{\text{pw}}$  is shifted very little from its value in the smaller slit (Fig. 3) whereas capillary condensation is shifted to significantly smaller  $\Delta\mu$ . The estimates of the latter from both the Clapeyron and the modified Kelvin equations lie within 8% of the result of the full calculation.

Using the Clapeyron equation for both the prewetting (where  $\alpha$  denotes thick and  $\beta$  denotes thin) and capillary condensation (where  $\alpha$  denotes “liquid” and  $\beta$  denotes thick “gas” film) coexistence curves allows us to extrapolate them down in temperature to locate the triple point for  $M = 61$ . This method locates the triple point to an accuracy of about 5% for  $T_\tau/T_c$  and a few thousandths in  $\mu/k_B T_c$ . Thermodynamic integration gives roughly the same degree of accuracy. We have found that the

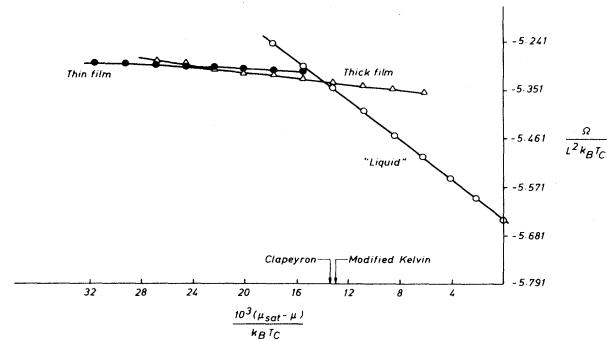


FIG. 4. The reduced thermodynamic grand potential  $\Omega$  as a function of chemical potential for a system of 61 layers and  $T = 0.652T_c$ . The arrows indicate the predictions of the modified Kelvin and the Clapeyron equations for capillary condensation.

most precise way of locating the triple point is to prepare by hand a starting configuration which consists of equal thirds of thick film, thin film, and "liquid." Watching this configuration evolve with time at various state points, we have located that state point for which the configuration is stable over 1000 time steps. Neighboring state points differing by as little as 0.5% in  $T_r/T_c$  and  $10^{-4}$  in  $\mu/k_B T_c$  exhibited configurations which relaxed quickly to a single- or two-phase configuration. Using this method we calculate  $T_r/T_c = 0.588 \pm 0.003$  and  $\Delta\mu_r/k_B T_c = 0.01827 \pm 0.00012$ .

Figure 5 shows the average density profiles of the three phases taken from the triple-point configuration after 1000 time steps. The errors indicated included contributions due to the fact that the interface regions between the stable phases were not unambiguously defined. The grand potential of each phase is also indicated. We note that the overall shapes of the density profiles are remarkably similar to the mean-field results shown in Fig. 7 of Ref. 2. For the two layers adjacent to the wall, the densities in the thick film and the "liquid" are nearly the same. We find the thick film is slightly thicker and the thin film has much lower densities than the corresponding mean-field results. This is as expected since the latter refer to temperatures that are further from the wetting transition than are the present simulation results.

As we follow the prewetting line towards higher tem-

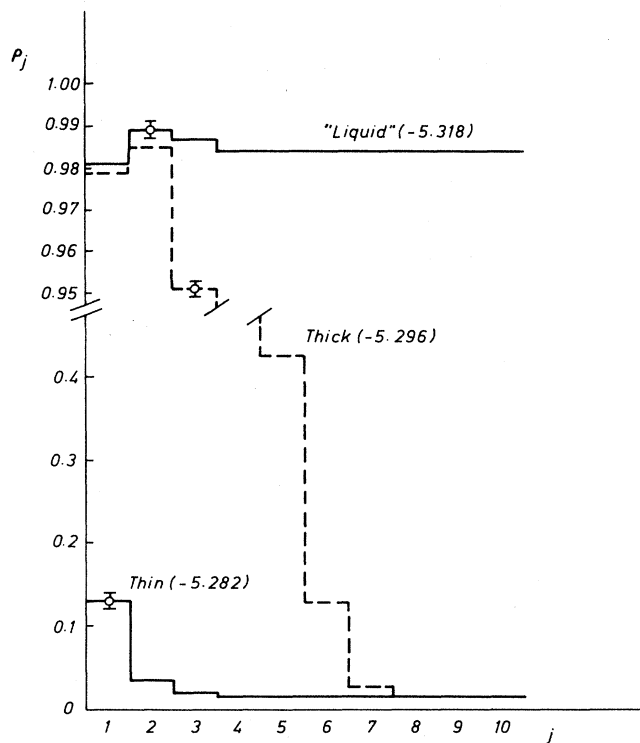


FIG. 5. The density profiles  $\rho_j$  for the triple-point state  $T = 0.588T_c$ ,  $\Delta\mu/k_B T_c = 0.01827$ ,  $M = 61$ . Only the first ten layers near one wall are shown. Representative error bars are indicated. The numbers in parentheses denote the reduced thermodynamic grand potential  $\Omega$  of each state.

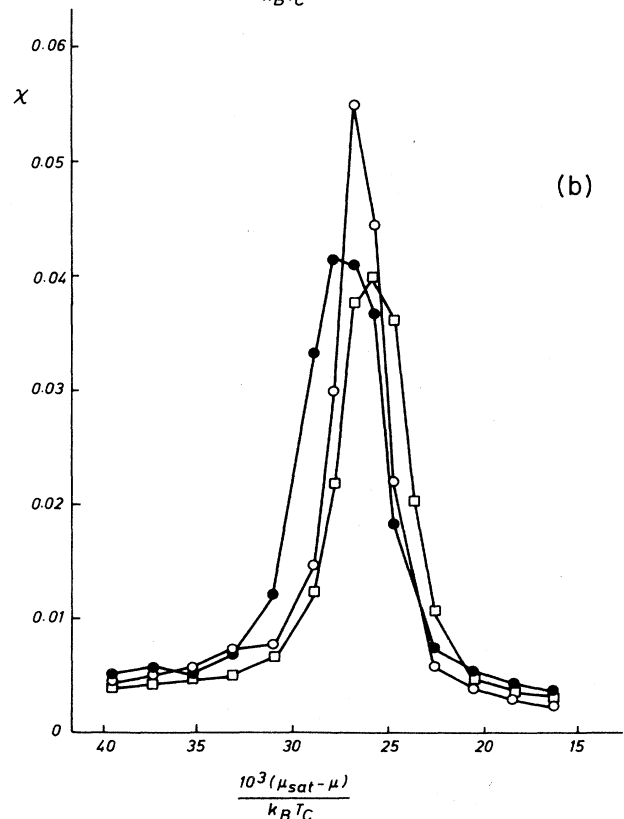
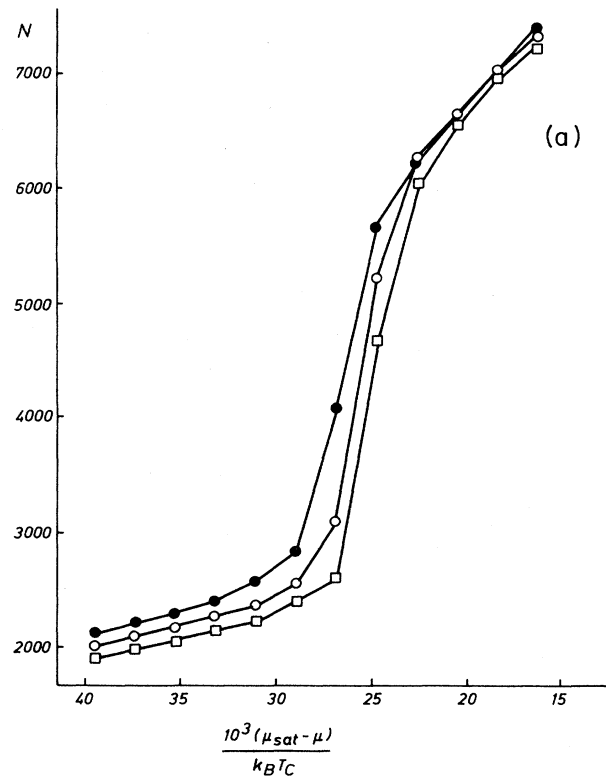


FIG. 6. (a) The integrated density as a function of chemical potential, for the three isotherms  $T = 0.713T_c$  ( $\bullet$ ),  $T = 0.708T_c$  ( $\circ$ ), and  $T = 0.703T_c$  ( $\square$ ).  $M = 61$ . (b) The susceptibility  $\chi$  as a function of chemical potential, for the same three isotherms as in (a).

perature we expect it to end in a prewetting critical point. We have observed continuous and reversible adsorption isotherms for  $T > 0.8T_c$  and “hysteresis loops” for  $T \leq 0.65T_c$ . However, the nature of hysteresis in a grand canonical simulation is complex, and such loops should be treated with some suspicion. They almost certainly indicate the failure of the simulation to sample adequately the appropriate phase space—because of limited simulation times. Moreover, finite-size rounding in the finite system must also be considered. Attempting to locate the critical point by searching for the disappearance of such loops is certainly problematical. An estimate of its location can be made by measuring the susceptibility  $\chi$  defined in (6b). For infinite wall area  $\chi = k_B T (\partial N / \partial \mu)_{T, M, A}$  will diverge at the critical point of a surface phase transition

Figures 6(a) and 6(b) show the average particle number  $N$  and susceptibility for three isotherms, all of which showed reversible behavior on a time scale of the simulation (50 000 time steps for each data point). While a complete analysis of the prewetting critical point would require studying the size dependence of  $N$  and  $\chi$ , the results of Fig. 6(b) suggest the critical temperature is  $\approx 0.71T_c$ . Since there was no hysteresis in any of the isotherms in Fig. 6(a) this reinforces the idea that inspection of the shape of  $N$  versus  $\mu$  isotherms is not a very reliable way of locating the critical point. The results of Fig. 6(b) do not, of course, demonstrate that we have determined accurately the location, or the nature, of the prewetting critical point. An extensive finite-size analysis is presently under way which should enable us to obtain an accurate description. We recall that it is conjectured that the prewetting critical point and, indeed, *all* critical points of surface transitions out of bulk coexistence, are two-dimensional Ising-like; the order parameter is the difference ( $N_\alpha - N_\beta$ ) and the correlation length can only diverge parallel to the walls.

#### IV. DISCUSSION

The results of our Monte Carlo simulations confirm the earlier predictions concerning the nature of the competition between the shifted bulk and the surface phase transition in a confined system. We have not attempted a direct comparison of simulation and mean-field results as there is no reason to suppose that the latter will be particularly accurate, especially for the prewetting surface. Nevertheless, the gross features do seem to be well reproduced by a mean-field approach, so that the overall form of the phase diagram in Fig. 1(a) is probably correct.

Perhaps the most striking feature in the confined system is the existence of a line of triple points. We have located one of these points for a slit with  $M = 61$  layers. Clearly, other triple points will occur for other values of  $M$ . It is important to recognize that the three phases which coexist are fluids. We deliberately chose to focus on the prewetting transition in the lattice-gas model, by choosing a wall potential of moderate strength and thereby avoiding the sequence of layering transitions that occurs with stronger walls, so that we mimic closely the corresponding transition in a continuum fluid at an inert

adsorbing substrate. Then the first-order wetting transition (at a single wall) occurs at a temperature  $T_w > T_R$ , the roughening temperature of the lattice—a situation which mimics a wetting transition above the bulk triple-point temperature in the continuum case; there the liquid-gas interface is always rough. Thus our results also have relevance for the continuum case.

That a simple one-component system should exhibit triple points with three coexisting fluid phases is, at first sight, surprising. The explanation<sup>6</sup> is clear from the thermodynamic relation (4). There are *two* additional contributions to  $d\Omega$  which are not present for bulk fluids. The surface tension term  $2\gamma dA$  allows coexistence of two surface phases (thick and thin film in the present case) out of bulk coexistence while the solvation-force term  $-(Af)dH$  allows the third phase (capillary-condensed “liquid”) to coexist at the same chemical potential. In other words, the usual Gibbs phase rule for a one-component bulk fluid is augmented by the two extra field variables. The same argument gives the possibility of other triple points. For example, first-order layering transitions, where the coverage increases in monolayer steps, persist in confined lattice gases.<sup>2</sup> These also compete with capillary condensation and can give rise to triple points where an  $m$  layer,  $m + 1$  layer, and a dense “liquid” coexist. It is possible that equivalent triple points also exist for continuum fluids confined between strongly adsorbing substrates.<sup>15</sup>

To the best of our knowledge this is the first time that capillary condensation has been investigated in simulations of lattice models. There is a growing literature on simulation of continuum fluids in model pores<sup>16</sup> and the validity of the Kelvin equation for condensation has been tested in that work. However, the large majority of these continuum simulations refer to fluids inside cylindrical capillaries for which a true phase transition should not occur. Consequently, there are some difficulties in interpreting the results<sup>15</sup> associated with the precise nature of the observed metastability and the finite-size rounding of the transition. Our present results for condensation are not beset by such problems. They are consistent with those for the “quasi” transition in cylinders and with the various mean-field tests of the Kelvin equation.<sup>1,2</sup> We find that the latter severely underestimates the shift in the bulk transition—even in a slit as large as 61 layers—when thick adsorbed films are present. Incorporating the Derjaguin correction for the effects of the wetting films appears to improve matters—at least for the two temperatures reported here. For smaller slits, however, even the modified Kelvin equation provides poor estimates of the shift. We note that some of the uncertainties involved in making the Kelvin estimate, i.e., extrapolating to  $\mu_{\text{sat}}$ , could be avoided if independent data were available for the liquid-gas surface tension  $\gamma_{\text{gl}}$  at the temperature of interest. In a complete wetting situation ( $T > T_w$ ), at bulk coexistence,  $\gamma_{\text{wg}} - \gamma_{\text{wl}} = \gamma_{\text{gl}}$ . Mean-field results<sup>1,2</sup> suggest that the Kelvin equation is much more accurate in a partial-wetting situation ( $T < T_w$ ) where  $\gamma_{\text{wg}} - \gamma_{\text{wl}} = \gamma_{\text{gl}} \cos\theta$ , with contact angle  $\theta > 0$ . We performed simulations for such a situation by choosing the “9-3 continuum” approximation for the wall potential:

$$V_s(z) = \frac{R\epsilon\pi}{45} \left[ \left( \frac{a}{z} \right)^9 - 15 \left( \frac{a}{z} \right)^3 \right]. \quad (9)$$

For the same choice,  $R = 0.31$ , as previously (9) has a much weaker attractive minimum than (2) and the walls remain partially wet up to the highest temperatures we investigated, i.e.,  $T = 0.9T_c$ . At this temperature we observed capillary condensation from a "gas" with only thin adsorbed films at the walls to "liquid" at  $\Delta\mu/k_B T_c = 0.00084 \pm 0.0002$  for a slit with  $M = 31$  layers. The Kelvin estimate is easier to make now as the metastable-gas branch persists to  $\mu_{\text{sat}}$  in partial wetting and we found  $\Delta\mu_K/k_B T_c = 0.00099$ . The transition occurs very close to bulk coexistence since  $\cos\theta$  is only slightly greater than zero. Mean-field calculations were carried out<sup>17</sup> for the same potential and these predict  $\cos\theta = -0.34$  for  $T/T_c^{\text{MF}} = 0.9$  (Ref. 18) ( $T_c^{\text{MF}} = 3\epsilon/2k_B$  is the mean-field critical temperature). Thus in mean field the bulk coexistence curve is shifted to  $\mu > \mu_{\text{sat}}$  and capillary *evaporation* occurs for a weakly supersaturated fluid. In this case the result of the full mean-field calculations lies within 1% of the Kelvin estimate for  $M = 31$ . How the bulk phase transition is affected by confinement depends crucially on the wetting behavior at a single wall. If the contact angle is not described accurately by mean field (in a given temperature range) the latter approximation may give qualitatively incorrect predictions for capillary condensation.

There are several features of the phase diagram (Fig. 1) that we have not yet been able to investigate by simulation. The capillary-condensation surface is bounded by a line of capillary critical points which correspond to shifted bulk critical points.<sup>1,2</sup> In the limit  $M \rightarrow \infty$ , scaling arguments<sup>19</sup> predict that the critical temperature of the fluid is shifted by an amount  $\Delta T_c \sim M^{-1/\nu}$  where  $\nu$  is the bulk-correlation-length exponent;  $\nu = 0.63$  for the  $d = 3$  Ising model. Checking this prediction for slits as wide as 61 layers is very difficult. We note, however, that shifts of the bulk critical point, consistent with the predictions of finite-size scaling, have been determined in simulations<sup>20</sup> of Ising films, with *free boundaries*, for  $M$  in the range 2–20 layers. The critical points become two-dimensional-like. Finally, we remark that the prewetting line and its critical point should, in principle, depend very weakly upon  $M$ . Our present simulations were not able to detect any shift of this line.

#### ACKNOWLEDGMENTS

We are grateful to C. J. Howls for carrying out the mean-field calculations in Ref. 17 and making the results available to us. We have benefited from conversations with M. P. Allen and A. O. Parry. This research was supported by the Science and Engineering Research Council of the United Kingdom, whose Computational Science Initiative provided a grant for the purchase of the Active Memory Technology DAP 510.

- <sup>1</sup>R. Evans, U. Marini Bettolo Marconi, and P. Tarazona, *J. Chem. Phys.* **84**, 2376; *J. Chem. Soc. Faraday Trans. 2* **82**, 1763 (1986). These papers include brief reviews of earlier work on the phase equilibria of confined fluids and of adsorption in model pores.
- <sup>2</sup>E. Bruno, U. Marini Bettolo Marconi, and R. Evans, *Physica A* **141**, 187 (1987).
- <sup>3</sup>R. Evans and U. Marini Bettolo Marconi, *Phys. Rev. A* **32**, 3817 (1985).
- <sup>4</sup>J. W. Cahn, *J. Chem. Phys.* **66**, 3667 (1977); C. Ebner and W. F. Saam, *Phys. Rev. Lett.* **38**, 1486 (1977).
- <sup>5</sup>C. Ebner, *Phys. Rev. A* **22**, 2776 (1980); **23**, 1925 (1981).
- <sup>6</sup>R. Evans and U. Marini Bettolo Marconi, *J. Chem. Phys.* **86**, 7138 (1987).
- <sup>7</sup>A. K. Sen and C. Ebner, *Phys. Rev. B* **33**, 5076 (1986). Prewetting has also been observed in simulations of Ising models with short-ranged wall forces—see Ref. 14.
- <sup>8</sup>Evidence for a prewetting transition has been found very recently in constant  $N, p, T$  Monte Carlo simulations of a Lennard-Jones model of fluid argon at a  $\text{CO}_2$  substrate. J. Finn and P. A. Monson (private communication).
- <sup>9</sup>G. S. Pawley, R. H. Swendsen, D. J. Wallace, and K. G. Wilson, *Phys. Rev. B* **29**, 4030 (1984).
- <sup>10</sup>D. Nicholson and N. G. Parsonage, *Computer Simulation and the Statistical Mechanics of Adsorption* (Academic, New York, 1982), Chap. 3.
- <sup>11</sup>B. K. Peterson and K. B. Gubbins, *Mol. Phys.* **62**, 215 (1987).
- <sup>12</sup>R. Evans and U. Marini Bettolo Marconi, *Chem. Phys. Lett.* **114**, 415 (1985).
- <sup>13</sup>B. V. Derjaguin, *Acta Phys. Chem.* **12**, 181 (1940). Derjaguin also showed that for finite-ranged or exponentially decaying wall potentials the correction is  $M - 2ta^{-1}$ , as would be expected from purely geometrical considerations.
- <sup>14</sup>K. Binder and D. Landau, *Phys. Rev. B* **37**, 1745 (1988).
- <sup>15</sup>P. C. Ball and R. Evans, *J. Chem. Phys.* **89**, 4412 (1988).
- <sup>16</sup>See Ref. 11 and B. K. Peterson, K. E. Gubbins, G. S. Heffelfinger, U. Marini Bettolo Marconi, and F. van Swol, *J. Chem. Phys.* **88**, 6487 (1988), and references therein.
- <sup>17</sup>C. J. Howls (unpublished).
- <sup>18</sup>The mean-field results of Ref. 17 show  $\cos\theta$  decreasing for  $T > 0.9T_c^{\text{MF}}$  with the possibility of a transition to complete drying ( $\cos\theta = -1$ ) close to the critical temperature.
- <sup>19</sup>E.g., H. Nakanishi and M. E. Fisher, *J. Chem. Phys.* **78**, 3279 (1983), and references therein.
- <sup>20</sup>K. Binder, *Thin Solid Films* **20**, 367 (1974). An excellent review of finite-size effects on both first- and second-order transitions is given by K. Binder, *Ferroelectrics* **73**, 43 (1987).