Nucleation of fluids confined between parallel walls: A lattice Monte Carlo study

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Nucleation phenomena in lattice gas models of simple and chain molecules confined in slitlike pores are studied using Monte Carlo methods. Finite-size scaling is used to investigate the nature of phase transitions accompanying the formation of layers at the pore walls. It is demonstrated that nucleation leads to the symmetry breaking and the formation of nuclei at one wall only.

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I. INTRODUCTION

The formation of finite clusters in supersaturated vapors is a well-established phenomenon [1–3], which has been intensively studied by computer simulation methods [4–6], despite serious problems and difficulties. Among these problems are the inherent instability of small clusters in an open system and finite-size effects [4,7]. One of the consequences of finite-size effects is the formation of droplets of different shapes [8,9]. At low densities the circular (spherical) droplets minimize the interfacial contribution to the free energy in two (three) dimensions. At higher densities the coexisting phases consist of bands or rings around the periodic torus.

The phase behavior of confined fluids differs from that of bulk fluids. Capillary condensation merely involves modification of the bulk transitions, but wetting and layering transitions arise solely from the presence of wall-fluid interfaces. Nucleation is a precursor of the first-order transition. It is a thermally activated process that depends exponentially on the height of the free-energy barrier associated with the formation of the critical nucleus [10]. This barrier is very sensitive to even small changes in environment—e.g., the presence of walls.

Recently, the results of molecular dynamics simulations of nucleation in slitlike pores were reported [11,12]. It was found that the strength of the fluid-wall attractive interactions can strongly affect the process of nucleus formation. If the attraction is very weak, nuclei tend to form in the interior of the pore. When the attraction is strong, nuclei are formed at the walls and their formation originates from two sources: surface diffusion of adsorbed particles at the wall and the deposition of clusters formed in the interior of the pore. The change of the mechanism of nucleation at a single wall due to the change of the fluid-wall attraction was also stressed by Toxvaerd [13]. He found that for weak adsorbing potential a depletion zone at the wall appears and the heterogeneous nucleation is suppressed. Quite recently, Page and Sear [14] used Monte Carlo simulations to study the nucleation in slitlike pores closed at one end and found that the nucleation often proceeds via two steps: nucleation inside the pore and nucleation outside the pore. The rates of these two nucleation processes have opposing dependences on the pore size, resulting in a characteristic pore size at which the nucleation rate of the new phase is maximal.

The extension of density-functional-type approaches to study the properties of critical nuclei formed in slitlike pores was presented in Refs. [15–17]. It was shown that in the case of capillary condensation the critical nucleus can either be attached to one of the planes or can bridge the two planes, depending on the intermolecular interactions and thermodynamic conditions. In other words, the nucleation may lead to symmetry breaking in the system. We note that the symmetry breaking was also observed in the density functional calculations of confined Lennard-Jones fluids under constraint of a constant density [18,19]. The thermodynamic conditions were such that the fluid at a single wall underwent the first-order prewetting transition; at higher temperatures, only symmetric profiles were observed. In our opinion the behavior of density profiles observed in Refs. [18,19], as well as in the former canonical ensemble molecular dynamics simulations [20,21], was driven by the nucleation phenomena.

In the case of strong fluid-wall interactions the capillary condensation may be preceded by a series of first-order layering transitions, which take place at the slit-pore walls. Computer simulations for lattice gas models demonstrated that the critical temperatures of layering transitions within consecutive layers increase, but the differences between them may be very small [22,23]. Therefore the nucleation in such systems may be a quite complex phenomenon that involves first-order transitions within consecutive layers.

In this work we apply lattice model and Monte Carlo simulations to study the layering transition and the nucleation within the first layer adjacent to both walls forming a slitlike pore. Two models are considered. The first one is just a simple lattice gas in a slit whose walls are at a distance large enough to ensure that layering transitions at the opposing surfaces are uncorrelated. Next, we consider the system in which the confined molecules are chains on a cubic lattice. In this case the pore width is smaller than twice the chain length and thus the transitions at the two pore walls are correlated. In other words, we intend to study the systems without and with correlations of the transitions at the opposing walls. Moreover, the choice of the system involving chain particles has been stimulated by our recent density functional study of similar off-lattice systems. We have demonstrated that under certain thermodynamic conditions the density functional approach may lead to symmetry breaking in the system and to unusual phase diagrams [24]. One plausible explanation of the observed behavior was the nucleation of chain molecules at one pore wall.

II. MONTE CARLO SIMULATION

We consider a lattice of cubic symmetry. The system is delimited from top and bottom by impenetrable walls that constitute the planes $i=0$ and $i=H+1$, respectively. The size of the system in the directions parallel to the walls is $L\times L$. In the first case we study layering transition in a simple lattice gas confined in the pore of $H=4$ layers wide. The selected wall-to-wall distance is large enough to consider the layering at each wall as independent of the transition at another wall. Only the interactions between nearest neighbors are assumed, and the energy of each interacting pair is ε. The energy of adsorption of particles located within the layers adjacent to the walls is 2ε and zero for all remaining layers.

The second system consists of chains built of $M=6$ segments whose first segment $J=1$ is pinned within the first layer at one of the walls. In the case of all remaining segments, $2\leq J\leq M$, the segment-wall interaction is zero when the segment is located in any of the layers $i=1,2,\ldots,H$. Of course, the segments cannot penetrate the walls, and hence the segment-wall interaction is equal to infinity for $i=0$ and $i=H+1$. The pinning of one of the terminating segments to one of the pore walls does not mean that these segments cannot move in the OXY plane. In fact, the movement of those segments in the direction parallel to the pore walls was allowed and, moreover, those segments were allowed to "jump" between the walls. The assumed model mimics the off-lattice model studied in Ref. [24].

The pore width has been fixed and assumed to be equal to $H=8$. Each segment of a chain interacts only with its nearest neighbors (including the neighbors belonging to the same chain) with the energy ε. The pore is narrower than $2M$; therefore, the straightened chains located at one pore wall feel the presence of segments located at another wall. Thus, in contrast to the previous case, the phenomena occurring at opposite walls are not independent.

Both models were studied by Monte Carlo (MC) simulation methods. To estimate the location of phase boundaries, simulations in the grand-canonical MC (GCMC) ensemble, using a hyperparallel tempering algorithm, were performed. Our calculations followed the method described in Ref. [25]. However, the majority of runs were carried out in the canonical MC (CMC) ensemble using a parallel-tempering technique, outlined in Refs. [25–27], and with Rosenbluth and Rosenbluth's bias for chain molecules [28]. To facilitate finite-size scaling analysis cells of L ranging between 20 and 80 were used.

Our preliminary simulations indicated that the nucleation in the pore leads to asymmetric density profiles. In order to monitor the symmetry breaking we introduced the order parameter

$$\Psi = (N_1 - N_H)/(N_1 + N_H), \tag{1}$$

where N_i is the number of molecules (for lattice gas) or segments (for chains) pinned at opposing walls, $i=1$ and $i=H$. This order parameter indicates whether there occurs the formation of phases of different densities at different walls. In order to investigate the nature of the phase transitions, we calculated the susceptibility conjugated with our order parameter,

$$\chi_L = NkT[\langle\Psi\rangle^2 - \langle\Psi^2\rangle], \tag{2}$$

where $\langle\cdots\rangle$ denotes the canonical ensemble average. In the case of a first-order transition the maximum value of susceptibility scales with the system size as [29–31]

$$\chi_{\max,L} \propto \chi_0 + \alpha L^D, \tag{3}$$

where $\chi_{corr}(L)=\chi_{\max}(L)-\chi_0$. The values of χ_0 can be estimated from the plot of $\chi_{\max}(L)$ versus L^D by extrapolating the data to $L=0$. Of course, the system dimensionality D equals 2 in our case. The information about the structure of different phases was also obtained from a direct inspection of snapshots.

We have also carried out some auxiliary (and limited in their extent) calculations for a slightly modified model involving chains. The pinning of the first segments within the layers adjacent to the pore walls means that their adsorption energy is infinite. The modification relied on the assumption that the energy of the interaction of the first segments located within the first wall was very large, but finite (e.g., 10ε). The results obtained for the original and for the modified models were very close, but the convergence of the results in the latter model was much slower.

III. RESULTS AND DISCUSSION

We begin with a presentation of selected results of GCMC simulations for the lattice gas in a slitlike pore. Parts (a)–(c) of Fig. 1 present unweighted histograms $P(\rho)$ obtained for the systems of different sizes: namely, for $L=10$, 20, and 40, respectively. In the above ρ is the average density, equal to $\rho=N/(H\times L^2)$, and N is the total number of confined lattice gas particles.

The histograms presented in Fig. 1 have been recorded at $T^*kT/\varepsilon=0.51$, 0.54, 0.57, and 0.60 and at the chemical potential at the coexistence for the layering transition in the layers adjacent to both pore walls ($\mu/\varepsilon=-4.0$). The critical temperature of this transition equals $T^*\approx 0.567$ and results from the fact that the lattice gas model can be mapped onto the Ising model [32]. Since the coupling constant of the two-dimensional lattice gas is equal to one-fourth of that corresponding to the Ising ferromagnet, the critical temperature of the two-dimensional lattice gas is also 4 times smaller than the critical temperature of the two-dimensional Ising ferromagnet [33].

At low temperatures the system fluctuates between states corresponding to almost empty (gaslike) and almost completely filled (liquidlike) layers at two pore walls (the inner layers are always almost completely empty). However, in addition to the two peaks on the histograms that reflect the existence of the above-mentioned phases, we observe the appearance of the third peak at $\rho=0.25$. This peak does not vanish when the system size increases and corresponds to a filled layer at one wall and an empty layer at the second wall; therefore, it characterizes an "intermediate" stage between the gaslike and liquidlike coexisting phases.

The simulations of the nucleation have been carried out in the canonical ensemble, keeping the number of confined par-

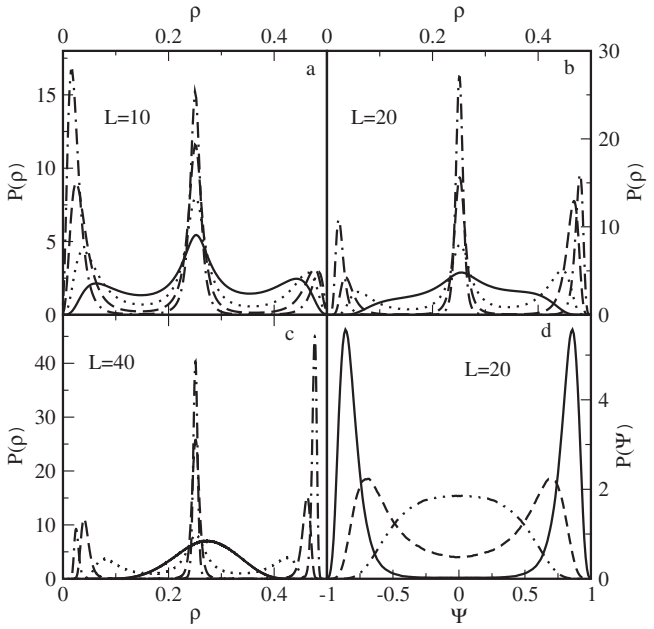

FIG. 1. Parts (a)–(c): the distributions $P(\rho)$ from GCMC simulations for the system sizes given in the figure and for $\mu/\varepsilon=-4.0$. The curves are at $kT/\varepsilon=0.6$ (solid lines), 0.57 (dotted lines), 0.54 (dashed lines), and 0.51 (dash-dotted line). Part (d) shows examples of the distributions $P(\Psi)$ from CMC simulations at $\rho=0.125>$, $\mu/\varepsilon=-4.0$, and $kT/\varepsilon=0.6$ (dashed line), 0.55 (dotted line), and 0.5 (solid line).

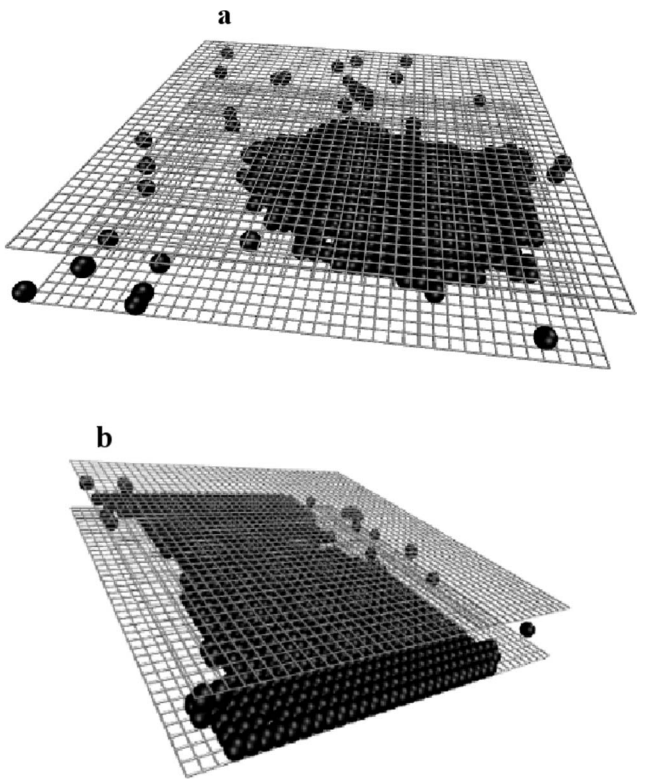

FIG. 2. Examples of snapshots from CMC simulations at $kT/\varepsilon=0.5$. Part (a) is for $\rho=0.175$ and part (b) is for $\rho=0.075$.

ticles constant. We concentrated on studies of the behavior of the order parameter Ψ that just describe symmetry breaking in the system. Figure 1(d) shows an example of the distribution $P(\Psi)$. The functions $P(\Psi)$ were obtained for a system size of $L=20$ and for a density $\rho=0.125$, which corresponds to the situation of only one layer being half-filled. Of course, at temperatures higher than the critical temperature of the first layering transition the distribution of confined particles is symmetric inside the pore and thus $P(\Psi)$ at $T^*=0.6$ is centered around $\Psi=0$. At $T^*=0.5$ and 0.55 the histograms clearly demonstrate that the system "jumps" between two configurations, each connected with the formation of a liquidlike structure at one of the walls and a gaslike structure at another wall. In other words, the formation of nuclei occurs at one wall only and the system loses its symmetry.

For $\rho\leq 0.25$ (i.e., at densities lower than the density of a completely filled single layer) the formation of nuclei always occurs only within the layer adjacent to the pore wall. This is illustrated by the snapshots in Fig. 2. At low ρ nuclei of circularlike shape are present, while when ρ increases they assume the shape of stripes running along one of the axes parallel to the pore wall. For $\rho>0.25$ (for the sake of brevity the relevant figures have been omitted) the distributions $P(\Psi)$ are qualitatively similar to those from Fig. 1(d), The nuclei are still formed at one layer adjacent to the pore wall, while the layer at the second wall is almost completely filled. No formation of "droplets" on already adsorbed layer, which might lead to the formation of "bridges" connecting two walls, has been observed during our simulations.

In order to understand the nature of the nucleation we have plotted the dependence of $|\Psi|$ on temperature for various system sizes and for densities $\rho=0.075$, 0.375, and 0.25 [see Figs. 3(a)–3(c)]. For $\rho=0.075$ and $\rho=0.375$ [parts (a) and (b), respectively], the curves $|\Psi|$ vs T^* for different L cross. This behavior is characteristic [34] of the first-order

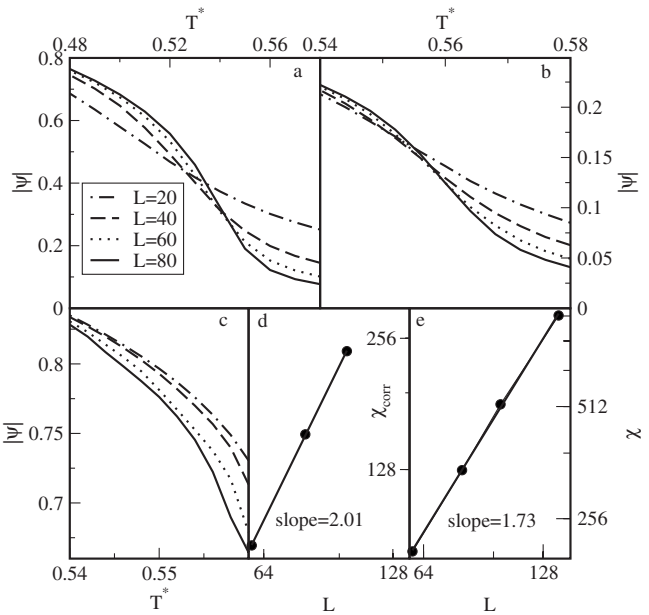

FIG. 3. Parts (a)–(c): the dependence of $|\Psi|$ on the temperature for different system sizes given in the figure. Part (a) is for $\rho=0.075$, part (b) for –0.375, and part (c) for 0.25. Part (d) shows the scaling of χ_{corr} for $\rho=0.15$ and part (e) the scaling of χ for $\rho=0.25$. The slope of the straight lines is given in the figure.

phase transition. However, for $\rho=0.25$ (i.e., for a density equal to the critical point density of the layering transition) the plotted curved do not cross; i.e., the transition is continuous [see Fig. 3(c)]. In fact, the scaling plots of the susceptibilities [Figs. 3(d) and 3(e)] clearly demonstrate that except for the critical density, $\rho=0.25$, the slope of the log-log plots is almost exactly equal to 2, the value characterizing the first-order transition for two-dimensional systems, whereas for $\rho=0.25$ the slope assumes a value characteristic of a continuous Ising-like transition [34]. This reflect the development of critical fluctuations in the system, and at the critical density the transition becomes of second order.

The above-presented results lead to conclusions that could be anticipated considering the properties of confined simple lattice models [35]. We have decided to include them here for the sake of a comparison with the behavior of more complex systems involving chain molecules in a confined geometry.

The second series of simulations have been carried out for confined chain molecules. The density ρ is now $\rho=NM/(H\times L^2)$, where N is the total number of confined chain particles; i.e., NM equals the average number of occupied lattice vertices in the confined system. The grand-canonical simulations [Fig. 4(a)] show the density distributions $P(\rho)$ and demonstrate the coexistence between two phases. Unlike for the lattice gas, we do not observe "intermediate" peaks on the histograms, for the system size used. In fact, that additional peak has occurred for smaller systems (for the sake of brevity the relevant plots are omitted), but it disappears when the system size increases. The reason is that the layers formed at opposing walls are not statistically independent. The histograms of Ψ obtained from canonical ensemble simulations [Fig. 4(b)] again show that the nucleation causes the symmetry breaking and the formation of "pinned" nuclei at one pore wall only.

Similarly as in the previous case, the crossing of the curves $|\Psi|$ versus the temperature for different system sizes indicates that the nucleation is the first-order transition [Figs. 4(c) and 4(d)]. We should note that the crossing of the curves $|\Psi|$ vs T is visible only if L is large enough. In particular, the system size $L=10$ is evidently too small [Fig. 4(c)] and therefore the log-log plots of the susceptibility were obtained for $L\geq 40$. For the investigated densities the slope of the plots $\ln \chi_{corr}$ vs $\ln(L)$ is very close to 2, as expected for the first-order transitions in effectively two-dimensional systems.

In order to understand the observed transformations we have inspected numerous snapshots of the generated configurations, examples of which are given in Fig. 5. The scenario of changes during the transition, gained from the snapshots analysis, is as follows. At low ρ the first-order transition is associated with the clusters formation at one of the walls. At very low densities the clusters assume circularlike shape and then transform into stripelike-shaped objects when the density increases. It should be emphasized that those clusters form only at one wall. When, however, the density exceeds the density corresponding to a completely filled layer at one wall, the clustering starts to occur at the second wall. Then, a similar sequence of clusters at the second wall appears.

At this point we would like to make some comments concerning the applied methodology and, in particular, on the possibility to study the nature of phase transitions between different (droplet and stripe) phases in the canonical ensemble, offered by the use of the order parameter given by Eq. (1). In the case of nucleation in strictly two-dimensional systems, like in the Ising model studied by Pleimling and Selke [5], the use of a canonical ensemble allows us to determine the structure and distribution of nuclei in the system, but does not allow us to make any predictions concerning the nature of phase transitions. In the case of systems with two walls, like those considered here, the situation is different. When the nucleation takes place at one wall, then the particles accommodated near the second wall can be treated as a sort of reservoir of particles. Then the situation resembles the conditions met when the grand-canonical ensemble is used. The order parameter, Eq. (1), which provides direct information about the asymmetry of particle distribution between the two sides of the slit, allows us to determine the order of the phase transitions observed, as demonstrated above. It is quite likely that the same, or similar, order parameters can be useful to study nucleation phenomena and phase transitions in different systems, using computer simulations in the canonical ensemble.

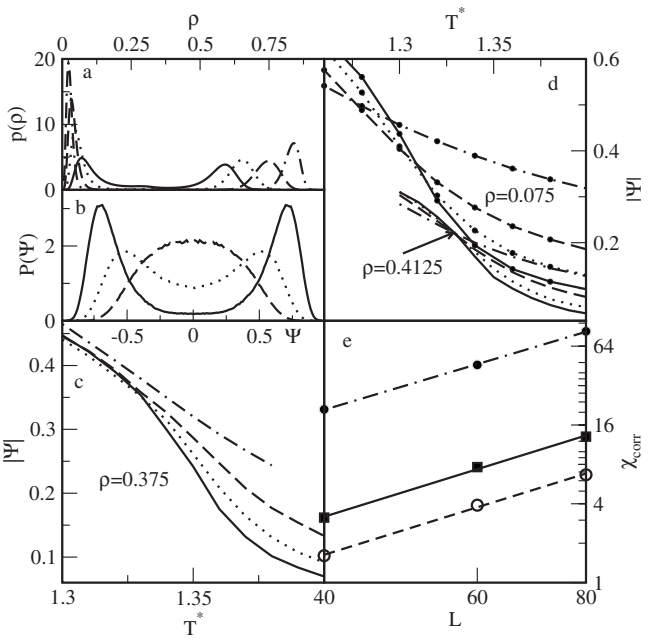

FIG. 4. The results of simulations of confined chain molecules. Part (a) shows examples of unweighted histograms $P(\rho)$ from GCMC simulations for $L=20$ and at $kT/\varepsilon=1.5$ and $\mu/\varepsilon=-3.4844$ (solid line), $kT/\varepsilon=1.46$ and $\mu/\varepsilon=-3.6345$ (dotted line), $kT/\varepsilon=1.42$ and $\mu/\varepsilon=-3.7965$ (dashed line), and $kT/\varepsilon=1.38$ and $\mu/\varepsilon=-3.9767$ (dash-dotted line). Part (b) presents the histograms $P(\Psi)$ obtained from CMC simulations for $L=40$ $\rho=0.075$ and at $kT/\varepsilon=1.25$ (solid line), $kT/\varepsilon=1.30$ (dotted line), and $kT/\varepsilon=1.35$ (dashed line). Parts (c) and (d) display the dependence of $|\Psi|$ on the temperature for different system sizes: $L=20$ (dash-dotted lines); 40 (dashed lines); 60 (dotted lines), and 80 (solid lines). The densities ρ are given in the figure. Part (d) shows the scaling plots of the compressibility for $\rho=0.225$ (dash-dotted line; the slope equals 1.98), $\rho=0.075$ (solid line; the slope equals 2.06), and $\rho=0.45$ (dashed line; the slope is 2.06).

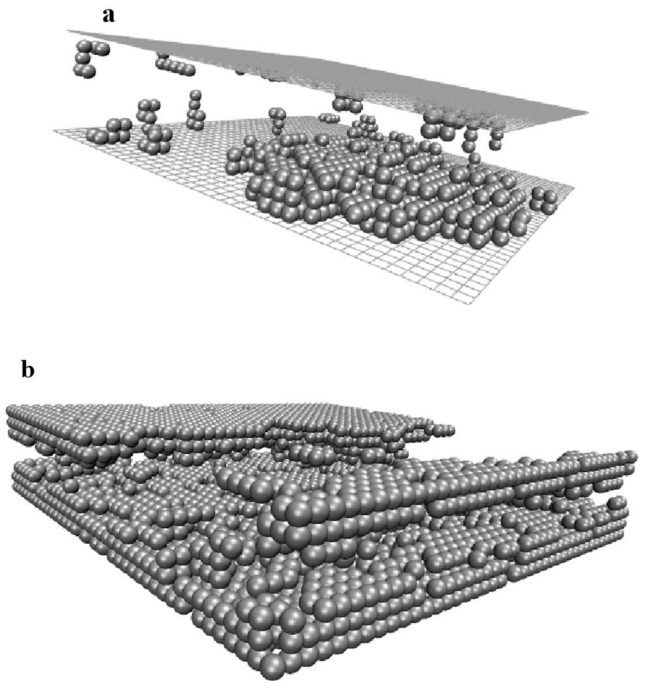

FIG. 5. Snapshots for chains in the systems of $L=40$, $kT/\varepsilon=1.25$, and $\rho=0.075$ [part (a)] and 0.45 [part (b)]. Note that for clarity we have omitted the wall lattices in part (b).

Let us summarize the results. Our simulations indicated that in the case of transitions within the layers adjacent to the slit-pore walls the formation of nuclei leads to a spontaneous symmetry breaking. The symmetry breaking is observed for both lattice models—i.e., for simple lattice gas as well as for chains pinned at the pore walls. For the first system the transitions at the opposing pore walls are uncorrelated. For the second model, the assumed length of the chains ($M=6$) and the chosen pore width ($H=8$) cause the layers formed at the walls to be not independent. In fact, they are expected to overlap. The lack and existence of the correlations leads to important differences between the nucleation mechanism in the two models considered. In the first model, three states corresponding to an empty slit, to the layer formed at one wall, and to two layers formed at opposing walls are equally probable at the chemical potential corresponding to the coexistence point. In the case of the second model, however, the correlations are expected to suppress the state with only one layer formed at one wall filled and therefore two stable states exist: two empty layers and two filled layers adjacent to the opposing walls.

In the models discussed here, the symmetry breaking is a result of the first-order nature of the transition. If the transition were of the second order, symmetry breaking would not occur. Therefore, we can expect that the nucleation scenarios described should hold if we are within the range of energies of adsorption corresponding to the wetting regime at a single wall. Confirmation of the above hypothesis, however, requires further extensive calculations.

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