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Wetting behavior of associating binary mixtures at attractive walls: A lattice Monte Carlo study

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The lattice gas model is used to study the effects of molecular association on the wettability of surfaces with attractive walls by binary symmetric associating mixtures. The model assumes that the adsorbate particles occupy a regular cubic lattice of sites and that the interactions between adsorbate particles involve only the first nearest neighbors. The energies of interaction between the pairs of like particles are the same, while the only interaction between a pair of unlike particles is due to association. Only the formation of dimers is allowed and the energy of association is finite. The particles are subject to the surface, van der Waals-like potential, assumed to be the same for both components. The model is studied with the help of the Monte Carlo simulation method in the grand canonical ensemble. Only the ground state properties are treated analytically. It is demonstrated that, in general, molecular association hinders wetting. In particular, in the systems with nonzero wetting temperature, the increase of the association energy leads to the increase of the wetting temperature and for sufficiently high energy of association the mixture does not wet the surface at all. When the system is expected to exhibit complete wetting at the ground state, the film formed by strongly associating mixtures wets the surface only at sufficiently low temperatures, below the dewetting temperature. It is demonstrated that the dewetting temperature increases with the strength of the surface potential as well as with the increase of the association energy.

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I. INTRODUCTION

The behavior of nonuniform binary mixtures in contact with a wall is a problem of great importance and is not quite well understood [1–7]. The main difficulties arising here are connected with a rather large number of parameters that define the interactions in nonuniform mixtures as well as with the multiplicity of thermodynamic paths that can be used. Even in the simplest possible lattice model with only nearest neighbor interactions, there are three parameters, which represent interaction energies between different pairs, and two parameters determining the strength of fluid-solid interaction for each component [4]. Under experimental conditions, the interactions between different pairs of adparticles are different. Also, the interaction of each component of the mixture with the solid substrate is different, and hence, one component is usually favored. The same assumption is also met in a majority of theoretical and computer simulation studies performed for adsorption of binary mixtures [5,6,8–11].

A particular problem that has recently been studied theoretically and with help of computer simulations concerns the adsorption of the so-called symmetric binary mixtures, characterized by the same interactions between pairs of like particles and by different energy of interaction between a pair of unlike particles, on nonselective, i.e., such that both components interact with the solid with the same energy, single walls [5,7,12] and in slitlike pores [13,14]. The wetting behavior of symmetric binary mixtures that are in contact with a nonselective wall has been also studied by Dietrich and Schick [5], by Schmid and Wilding [7], and quite recently by Bucior *et al.* [12]. It has been demonstrated that the surface films formed by mixtures, which undergo a demixing transition in the bulk, may exhibit quite complex behavior. In particular, various surface transitions have been found, including first-order and continuous demixing and prewetting transitions between films of different composition.

It is known that bulk associating binary mixtures exhibit quite different phase behavior than ordinary mixtures [15–19]. In particular, molecular association gives rise to the appearance of the so-called close loop liquid-liquid immiscibility and the existence of lower and upper critical solution temperatures. Also, the gas-liquid condensation in associating mixtures has been found to be considerably different [16,20]. In the systems with moderate association energies the condensed phase has been found to undergo gradual demixing transition at the temperature below the tricritical point, which is the onset of the λ line. Thus, at very low temperatures the gas-liquid condensation leads to the mixed condensed phase, while at higher temperatures it leads to a demixed condensed phase. In both cases the transition is of first order. Only above the tricritical point the demixing is a second-order transition. In strongly associating symmetric mixtures, the condensed phase is highly ordered and demixing does not occur. In consequence, the λ line does not exist and the condensation always occurs between two mixed phases, via a first-order transition [20].

The effects of confinement on the behavior of associating binary mixtures has been theoretically studied, but only in the framework of a mean-field-like density functional approach [19]. We are not aware of any study aiming at the elucidation of the effects of association on the wetting behavior of binary mixtures that are in contact with a solid. The studies of wetting at fluid-fluid interfaces, between two liquid phases, have demonstrated that the presence of association, or chemical equilibrium among the components, can lead to reentrant wetting as well as to dewetting transitions [21].

In this work we apply a very simple lattice gas model of a nonuniform reversibly associating symmetric binary mixture and discuss the problem of its wetting behavior in the case of a nonselective solid substrate. Although the model is very simple and can not be directly related to any real system, we believe that it captures the most essential features of associating binary mixtures that are in contact with a solid. We demonstrate that the wetting of solid surfaces by binary mixtures may be considerably influenced by molecular association. In particular, it is shown that the molecular association may lead to dewetting transition in the systems which exhibit complete wetting in the absence of associative interactions. The problem seems to be important since reversibly associating mixtures are common in nature and play a significant role in several technologically important processes. We are not aware of any theoretical as well as experimental studies that would demonstrate such effects.

The paper is organized as follows. In Sec. II, we present the model used, define the interaction potentials, discuss some basic aspects of its ground state properties and recall necessary information about the behavior of bulk systems. Then, in Sec. III, we describe the Monte Carlo method used. Section IV is devoted to the presentation of the results obtained for a series of systems characterized by different strength of the surface potential and by different energy of association. Section V summarizes our findings.

II. THE MODEL

The model of the fluid is the same as used in our earlier work [20], which was devoted to the investigation of bulk properties of associating symmetric binary mixtures. Thus, we consider a lattice gas model in which the particles of both components, *A* and *B*, occupy sites of a cubic lattice. A pair of particles interacts only when they occupy the first nearest neighbor sites. The energies of interaction between different pairs (AA, BB, and AB) are denoted by u_{AA}, u_{BB}, and u_{AB}. In the case of a symmetric mixture $u_{AA}=u_{BB}$, while, in general, u_{AB} is different. Besides, each particle *A* (*B*) has one acceptor (donor) that can participate in the formation of a dimer. Since the particles are structureless, the donors and acceptors do not have any prespecified locations. The association energy u_{as} is finite and hence the dimers are allowed to dissociate.

With the above assumptions, the Hamiltonian for such a bulk system can be written as

$$\mathcal{H}_b=u_{AA}\sum_{\langle ij\rangle} n_i^A n_j^A+u_{BB}\sum_{\langle ij\rangle} n_i^B n_j^B+u_{AB}\sum_{\langle ij\rangle} n_i^A n_j^B$$

$$+u_{as}\sum_{\langle ij\rangle} \gamma_{ij}-\mu_A\sum_i n_i^A-\mu_B\sum_i n_i^B, \qquad (1)$$

where n_i^K is the occupation variable equal to unity when the ith site is occupied by a particle of component K ($K=A$ or B), $\gamma_{ij}=1$ when both particles on sites i and j form a bond and equal 0 otherwise, μ_A and μ_B are the chemical potentials of both components. The first four sums run over all distinct pairs of nearest neighbors, while the last two sums are taken over all sites.

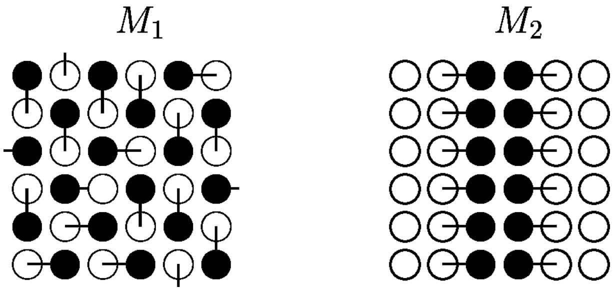

FIG. 1. The ordered mixed monolayer structures M_1 [part (a)] and M_2 [part (b)].

At the ground state, the above model predicts that under different conditions the condensed phase may be the one of pure phases consisting of particles *A* or *B*, or one of the two different mixed phases M_1 and M_2 of the structure schematically shown in Fig. 1. The phase M_1 is characterized by a random orientation of "bonds" resulting from the association, while in phase M_2 those bonds assume mutually parallel orientation.

Throughout this work we fix $u_{AA}=u_{BB}=-1$ and $u_{AB}=0$. Therefore, the only interaction parameter of the bulk fluid, which is allowed to change is $u_{as}^*=u_{as}/|u_{AA}|$, and we assume that it takes the values 0, -1, -2, -3 and -4. The same parameters have been used in the earlier study of bulk systems, for which the phase diagrams have been determined. Some knowledge about the properties and behavior of the bulk systems is a necessary prerequisite for the study of wetting phenomena. Therefore, we briefly recall here the information about the behavior of those bulk systems.

For $u_{as}^*=0$ and -1, the bulk behavior is qualitatively the same. In particular, when the gas condensation takes place along the path $\mu_A=\mu_B$ it leads to a demixed liquid. At the temperatures below the tricritical point it occurs via the first-order transition, while at higher temperatures along the λ line, it occurs via the continuous transition. For $u_{as}^*=-2$, the situation is more complex. At very low temperatures, below about $T^*=kT/|u_{AA}|=0.6$ the condensation is a first-order transition between the mixed gas and mixed condensed phase, of the structure M_2, as predicted by the ground state calculations. As the temperature increases, the condensed phase undergoes a gradual demixing, which completes at temperature of about $T^*=0.7$. The condensation remains the first-order transition up to temperature of about 0.86, where the tricritical point is located and the λ line begins. For $u_{as}^*=-3$ and -4, the gas condensation is always a first-order transition and leads to the formation of the mixed condensed phase M_2. It should be noted that the density of disordered fluid reaches quite high values, of the order of 0.8 at the temperatures just above about 0.86, for $u_{as}^*=-3$ and 0.84, for $u_{as}^*=-4$.

Next, we assume that the mixture is in contact with a solid attractive wall and that each component interacts with that wall via the van der Waals-like potential [22,23]

$$V_K(l)=V_{K,o}/l^3 \quad \text{when } K=A \text{ or } B, \qquad (2)$$

where l is the distance from the surface (expressed in lattice spacings) and $V_{K,o}$ is the fluid-solid interaction energy of particles K located in the layer adjacent to the solid surface. The Hamiltonian corresponding to the above defined nonuniform system reads

$$\mathcal{H}=\mathcal{H}_b+\sum_{l}\left[V_A(l)\sum_{i\in l} n_i^A+V_B(l)\sum_{i\in l} n_i^B\right], \tag{3}$$

where the first sum runs over different layers and the remaining sums run over all sites i which belong to layer l.

Depending on the values of both $V^*_{A,o}$ and $V^*_{B,o}$ ($V^*_{K,o}=V_{K,o}/|u_{AA}|$) the model may lead to quite complex surface phase behavior, involving layering transitions, which occur between states of different structure and number of occupied layers, prewetting and wetting transitions, as well as the demixing transition.

In a general case of a symmetric binary associating mixture with arbitrary values of the interaction parameters, u^*_{AB} and u^*_{as}, in contact with a nonselective wall, such that $V^*_{o,A}=V^*_{o,B}=V^*_o$, the only possible states of the adsorbed layer at zero temperature correspond to the film consisting of any number n of completely filled layers. The adsorbed film is in equilibrium with a bulk gas of density equal to zero. The state with the number of occupied layers $n=0$ represents the two-dimensional gas, which at $T=0$ has zero density.

When all of the n layers are filled by particles of only one component, the energy of the system (per lattice site) is equal to

$$e^*_{n,K}=(1-3n)+\sum_{i=1}^{n} V^*_o(i)-n\mu^*_K, \tag{4}$$

where $\mu^*_K=\mu_K/|u_{AA}|$ for both $K=A$ and B. Such a situation arises whenever the chemical potential of the other component is low enough (see the discussion below).

The other possibility occurs when the interaction between unlike particles u^*_{AB} and/or the association energy u^*_{as} is sufficiently large to induce the formation of mixed phases. In the case of a single occupied layer, the two different mixed phases, M_1 and M_2, (of the structure shown in Fig. 1) can appear. Those phases are the two-dimensional counterparts of the mixed phases found in bulk systems [20]. When the film consists of n layers of the phase M_1 or M_2, the corresponding energies are given by

$$e^*_{n,M_1}=(1-3n)u^*_{AB}+0.5nu^*_{as}+\sum_{i=1}^{n} V^*_o(i)-0.5n(\mu^*_A+\mu^*_B) \tag{5}$$

and

$$e^*_{n,M_2}=0.5(2-5n)+0.5n(u^*_{AB}+u^*_{as})+\sum_{i=1}^{n} V^*_o(i) -0.5n(\mu^*_A+\mu^*_B), \tag{6}$$

respectively. Of course, it is conceivable that under suitable conditions different sequences of occupied layers can appear. For example, on top of m layers occupied by one component, the next layers may be filled by the particles of another component, or by one of the above defined mixed phases M_1 or M_2. The expressions defining the energies of such films can be also readily obtained using the Hamiltonian (3).

From the ground state considerations of the bulk systems [20] it follows that the location of condensation and the structure of the condensed phase are determined by the values of both u^*_{AB}, u^*_{as} and the chosen path, i.e., the relation between the chemical potentials μ^*_A and μ^*_B. In the case of $u^*_{AB}=0$ considered here, the M_1 phase does not appear in the bulk, as well as in surface layers. The necessary condition for the presence of the M_2 phase reads $u_{as}<-1$ and the gas condenses to that phase always when the chemical potentials fulfill the condition

$$\mu^*_A+\mu^*_B=-5.0+u^*_{as} \tag{7}$$

and both μ^*_A and μ^*_B belong to the interval $[-3,-2+u^*_{as}]$. Beyond that region, only the pure A (when $mu^*_B<-2+u^*_{as}$) or B when ($mu^*_B<-2+u^*_{as}$) condensed phases appear, and the condensation point is located at $\mu^*_A=-3$ or at $\mu^*_B=-3$, respectively.

Whenever the surface potential fulfills the condition $V^*(1)-V^*(2)<-1$ [24], i.e., when $V^*_o<-1/0.875$, the formation of the adsorbed film proceeds via a sequence of layering transitions $n\rightarrow n+1$. This condition applies to the systems of an arbitrary value of the association energy. For weaker surface fields, the first layering transition, if it appears at all, involves a simultaneous condensation of more than one layer. Several examples of ground state phase diagrams for nonassociating mixtures have been presented in Refs. [10] and [11]. In the case of associating mixtures, those phase diagrams look quite similar, and only the structure of the mixed phase may be different. For example, when $V^*_o=-1.0$, the first layering involves condensation within the two layers adjacent to the solid, independent of the magnitude of u^*_{as}. The system with $u^*_{as}>-1$ corresponds to the situation in which any adsorbed layer is filled by only one component. In the case of $u^*_{as}<-1$, however, the model predicts the formation of mixed layers of the M_2 structure, just the same as in the case of a bulk phase. It should be noted that when the number of completed mixed layers, M_2, is even, the ground state energy of such a system is exactly the same as for the systems with alternating A and B layers.

Here, we assume that $V^*_{A,o}=V^*_{B,o}=V^*_o$ and restrict the discussion to relatively weakly adsorbing walls with $V^*_o\geqslant -1$. The condition for the complete wetting to occur at any temperature down to zero, depends on the type of the ground state phase diagram for the bulk mixture and the chosen path of approach to bulk condensation. When the bulk condensation leads to the formation of the pure, A or B, phases, a complete wetting at $T=0$ occurs whenever

$$\frac{u_{KK}}{V_{K,o}}<\sum_{l=1}^{\infty} l^{-3}, \quad K=A \text{ or } B, \tag{8}$$

and when the chosen path of the approach to bulk condensation is such that the chemical potential of one component is sufficiently low (e.g., see the discussion in Ref. [11]) when $\mu_A \to 3u_{AA}$ (bulk condensation to the pure K phase occurs at $\mu_K = 3u_{KK}$ ($K=A$ or B). On the other hand, when the bulk condensation leads to the formation of one of the mixed phases, M_1 or M_2, the corresponding conditions for a complete wetting along the path $\mu_A = \mu_B$ at $T=0$ are

$$\frac{u_{AB}}{0.5[V_{A,o}+V_{B,o}]\sum_{l=1}^{\infty} l^{-3}} < 1 \tag{9}$$

and

$$\frac{[u_{AA}+u_{BB}]}{[V_{A,o}+V_{B,o}]\sum_{l=1}^{\infty} l^{-3}} < 1, \tag{10}$$

respectively. The first case occurs whenever $u_{AB} < u_{AA} = u_{BB}$, while the second case occurs only when $u_{AB} > u_{AA}$ and $u_{as} < u_{AA}$. The growing adsorbed layer also assumes the M_1 or M_2 structure, respectively. Note that the above conditions (9) and (10) do not explicitly depend on the association energy, due to the cancellation of the corresponding bulk and surface contributions. With our choice of parameters, in particular, for $u_{AB}=0$, only condition (10) needs to be taken into consideration.

In the case of the computer simulation study one is, of course, forced to use finite systems and hence it is necessary to cut the surface potential at a certain finite distance l_{max}. In that case, the sums in the above equations, Eqs. (8)–(10), terminate at $l = l_{max}$. Here we assume that $l_{max}=5$, and hence, for the parameters chosen here, the value of V_o that delimits the regimes of complete and incomplete wetting at $T=0$ equals $V_{o,t} = 0.843\,41 u_{AA}$.

III. MONTE CARLO METHOD

Here we apply a standard Monte Carlo method in the grand canonical ensemble described in Refs. [8,20,24]. The simulation cell size was equal to $L_x \times L_y \times L_z$, with $L_x = L_y = 20$ and $L_z = 40$. Periodic boundary conditions in both x and y directions have been used, while in the z direction the simulation cell was closed with identical adsorbing walls located at $z=0$ and $z=41$. The use of such a slab geometry has already proved [9–11,23,25] useful and allows one to obtain better statistics, since one collects data from two surface regions. Of course, when the number of adsorbed layers increases it is possible that capillary condensation occurs. From our earlier experience it follows [23], however, that when the film thickness (at one wall) does not exceed one-fourth of L_z, it is possible to obtain quite reliable results and both surfaces appear to be statistically independent. A single Monte Carlo move, performed at a randomly chosen occupied site, consisted in an attempt to either annihilate the particle or to change its identity. In the case when the chosen site was empty, an attempt to create a randomly chosen particle A or B was performed. Also, the attempts to create or dissociate a dimer have been performed. All elementary moves have been accepted following the standard Metropolis criterion [24].

The bulk densities $\rho_{b,A}$ and $\rho_{b<B}$ of both components have been calculated as

$$\rho_{b,K} = \frac{1}{10}\sum_{l=16}^{25} \langle n_i^K \rangle, \quad \text{where} \quad K=A \text{ or } B \tag{11}$$

by assuming that the layers between 16 and 25 behave as a uniform system. The results have been compared with simulations performed for a uniform system, using the simulation cell of size $20\times20\times20$ and periodic boundary conditions applied in all three space dimensions. Those calculations have served not only as a check that the bulk densities have been accurately estimated, but also were used to determine bulk phase diagrams for the systems considered.

Then, the surface excesses of both components, $\rho_{ex,A}$ and $\rho_{ex,B}$, have been calculated as

$$\rho_{ex,K} = \frac{1}{2}\sum_{l=1}^{L_z} [\langle n_i^K \rangle - \rho_{b,K}], \quad \text{where} \quad K=A \text{ or } B. \tag{12}$$

The multiplier 1/2 arises from the fact that there are two surfaces present.

The surface excess densities of associates oriented parallel ($\rho_{ex,as}^h$) and perpendicular ($\rho_{ex,as}^v$) to the surface have been calculated in a quite the same manner.

The number of Monte Carlo steps (one Monte Carlo step consisted of $L_x \times L_y \times L_z$ elementary moves) used to calculate averages varied between 2×10^6 and 5×10^6 depending on the temperature and proximity to the bulk coexistence point and only every nth configuration was used. In general, a larger number of Monte Carlo steps and larger n must be used at the temperatures close to the second-order phase transitions, in order to minimize the effects of critical slowing down and increasing correlation time between subsequent configurations. In our calculations the values of n ranged between 5 and 50. A similar number of Monte Carlo steps was used for equilibrating the system.

IV. RESULTS AND DISCUSSION

In this section we present the results concerning adsorption of associating fluids at a series of surfaces characterized by different strengths of the surface potential, and, as already mentioned, we confine the discussion to the systems with V_o^* between -0.8 and -1.0. The properties of one-component systems characterized by such values of V_o^* have been already studied [25]. In particular, the systems with $V_{o,}^* > V_{o,t}^* = -0.84341$ (for $l_{max}=5$) exhibit nonzero wetting temperature, while for $V_o^* < V_{o,t}^*$ a complete wetting at any temperature, down to zero, occurs. The same conclusion stems from the ground state calculations for binary symmetric mixtures, discussed in Sec. II.

The first series of calculations have been performed for $V_o^* = -0.8$ and the basic results are presented in Fig. 2, which shows the adsorption isotherms obtained at different

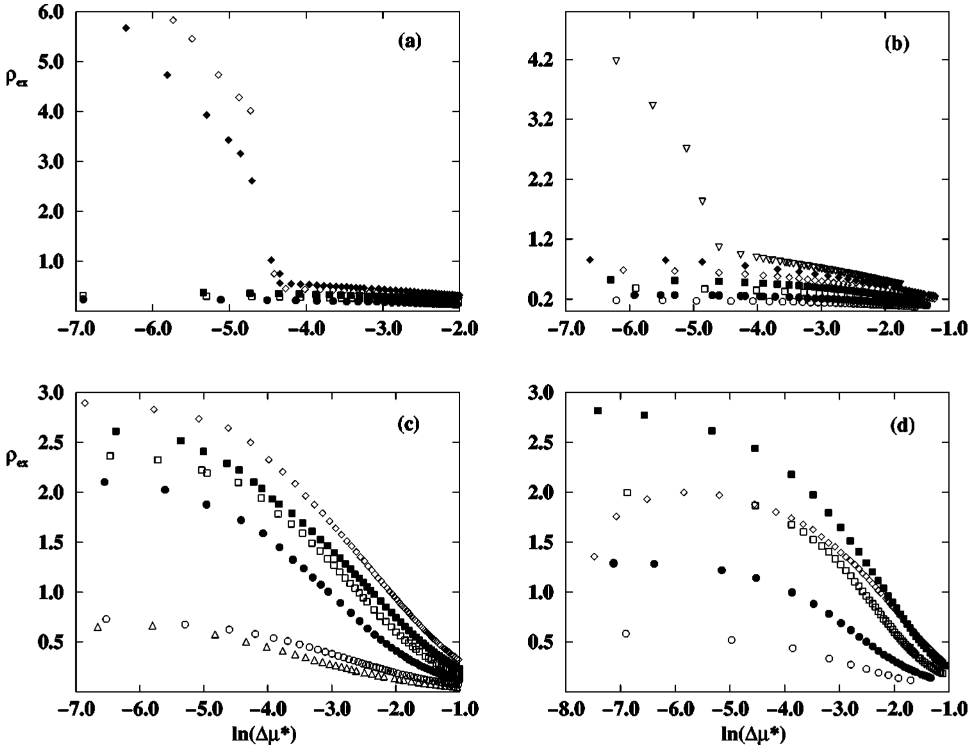

FIG. 2. Adsorption isotherms for the systems with $V_o^*=-0.8$ and different values of the association energy: $u_{as}^*=0$ (a), -1 (b), -2 (c), and -3 (d). The same symbols correspond to the same temperature in all panels: up triangles, $T^*=0.6$; open circles, 0.65; filled circles, 0.7; open squares, 0.75; filled squares, 0.8; open diamonds, 0.85; filled diamonds, 0.90; and down triangles, 0.95.

temperatures for the systems with various values of the association energy. In the case of $u_{as}^*=0$ [Fig. 2(a)] the isotherms calculated at temperature up to 0.8 correspond to the nonwetting regime, while in the case of the isotherms obtained at temperature $T^*=0.85$, and higher, a complete wetting takes place. In this case, the bulk phase diagram [20] exhibits the tricritical point at $T_{trc}^*\approx 1.18$ at which the first-order condensation transition meets the λ line, which corresponds to the continuous demixing transition. The increase of the association energy to $u_{as}^*=-1$ has already a large influence on the wetting transition temperature, which now occurs between 0.9 and 0.95 [Fig. 2(b)].

For still higher association energies equal to -2 and -3, the wetting remains incomplete up to the temperatures at which the bulk fluids attain high density at the coexistence [see Figs. 2(c) and 2(d)]. In particular, for $u^*=-2$ the adsorbed film reaches finite surface excess density a little lower than 3.0, at $T^*=0.85$. In this system the bulk tricritical point is located at only very slightly higher temperature of about $T_{trc}^*=0.865\pm 0.005$. The surface excess densities extrapolated to $\Delta\mu^*=0$ ($\Delta\mu^*=\mu_o^*-\mu^*$, where μ_o^* is the chemical potential at which the bulk condensation takes place) demonstrate clearly (see Fig. 3) that there are two different temperature regimes of the film growth. At the temperatures below 0.7, only a partially filled monolayer film occurs, while for higher temperatures the film thickness exhibits a jump, to ρ_{ex} about 2 and then grows nearly linearly with temperature. The appearance of those two regimes can be attributed to the changes in the structure of the condensed bulk phase with temperature [20]; namely, when $u_{as}^*=-2$ the bulk condensed phase undergoes a gradual demixing upon the increase in temperature, and this process occurs just over the temperatures between 0.65 and 0.7. The adsorbed film is mixed over the entire range of temperatures, and hence in the low temperature regime it coexists with a mixed liquid, while in the high temperature regime it coexists with already demixed liquid. This change in thermodynamic conditions leads to the observed changes in the film growth. When the association energy becomes still higher ($u_{as}^*=-3$), the condensed phase is mixed over the entire range of temperatures, and the bulk phase diagram has a different topology than that for lower association energies. Namely, it exhibits only the first order condensation between disordered and ordered (M_2) mixed phases, which at the temperatures above $T^*\approx 0.84$ are both quite dense. The adsorption iso-

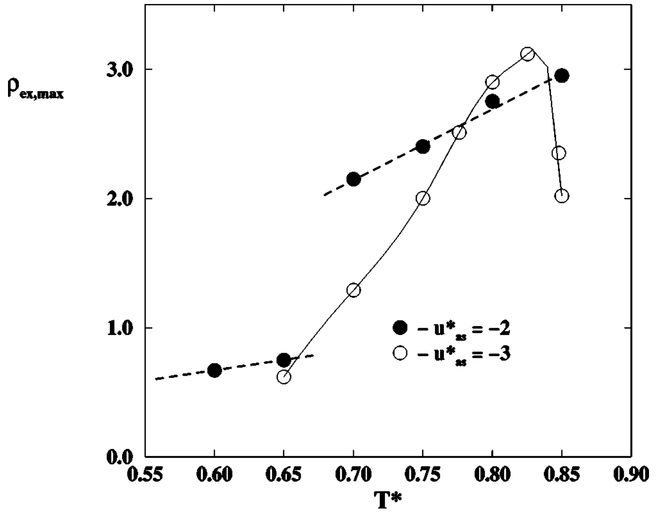

FIG. 3. The surface excess density at the bulk coexistence for the systems with $V_o^*=-0.80$ and the association energy $u_{as}^*=-2$ and -3.

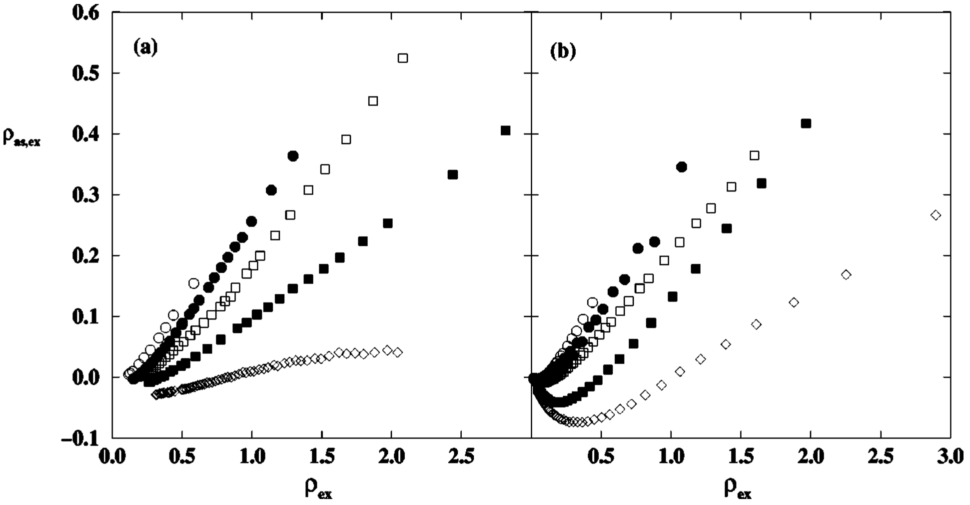

FIG. 4. The surface excess density of associates, $\rho_{ex,as}$, versus the total surface excess density, ρ_{ex}, at different temperatures (open circles, $T^*=0.65$; filled circles, 0.70; open squares, 0.75; filled squares, 0.80; and open diamonds, 0.85) obtained for the system with $V_o^*=-0.8$ and $u_{as}^*=-3$ [part (a)] and -4 [part (b)].

therms, shown in Fig. 2(d), clearly demonstrate that the film thickness remains finite at any temperature and that it gradually decreases on approaching bulk coexistence, when the temperature exceeds 0.83 (see Fig. 3). This is directly connected with a sudden increase of the fluid phase density close to coexistence, which reduces the surface excess density. In the case of $u_{as}^*=-4$, the results (not shown here) are quite similar to those obtained for $u_{as}^*=-3$. It should be noted that even for such high association energies the association within the adsorbed layers is rather limited (see Fig. 4) and the associates preferentially assume parallel orientation with respect to the surface (see Fig. 5). The data shown in Fig. 5 show that the surface excess of vertically oriented associates is negative.

Now, we turn to the discussion of systems characterized by higher values of $V_o^*=-0.85$, -0.9, and -0.95. For all these cases, the ground state calculations predict a complete wetting already at $T^*=0$. Figures 6–8 present the sets of adsorption isotherms obtained for the systems characterized by different V_o^* and for various values of the association energy. The systems with $u_{as}^*=0$ [cf. Figs. 6(a), 7(a), and 8(a)] behave as expected and do show complete wetting, preceded by multilayering transitions, associated with a simultaneous condensation of a number of layers, as predicted by the ground state calculations. For $V_o^*=-0.85$ that multilayering transition involves the condensation of the first four layers, while for $V_o^*=-0.9$ and -0.95, the condensation occurs in the first three layers. Indeed, the results presented in Figs. 6(a), 7(a), and 8(a), confirm the above prediction very well.

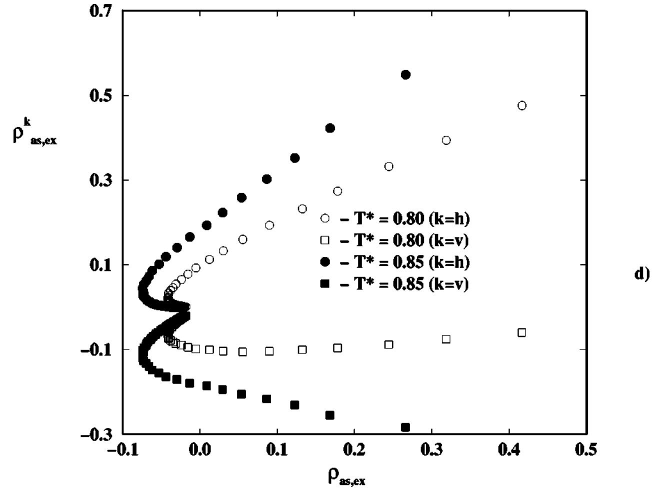

FIG. 5. The surface excesses of horizontally (h) and vertically (v) oriented associates, $\rho^k_{ex,as}$, versus the total surface excess density of associates, for the system with $V_o^*=-0.8$ and $u_{as}^*=-4$, at two different temperatures (shown in the figure).

The system with $V_o^*=-0.85$ and the association energy $u_{as}^*=-1$ shows similar behavior as that with $u_{as}^*=0$. Thus we observe a complete wetting, preceded by the condensation of the first four layers followed by a smooth growth of the adsorbed layer.

For $u_{as}^*=-2$ and $u_{as}^*=-3$, the adsorption stays finite on approaching bulk coexistence at all temperatures used here, quite similarly as in the case of the systems with $V_o^*=-0.8$. We have attempted to perform the calculations at still lower temperatures, below 0.6, but met very large metastability effects, so that even over some region of the chemical potential beyond the bulk condensation point the adsorption was very low. On the other hand, the ground state calculations lead to the conclusion that complete wetting should occur already at very low temperatures, $T^*=0$ included. Thus the results of our Monte Carlo simulations, performed at rather high temperatures, together with the ground state predictions, suggest that a dewetting transition should occur at temperatures below 0.6. At his point, however, we have no evidence for the existence of that transition.

The results obtained for the systems with $V_o^*=-0.9$ and the nonzero association energy are quite similar to those for $V_o^*=-0.85$ (cf. Figs. 6 and 7). The system with $u_{as}^*=-1$ exhibits the first layering transition involving mutual condensation in the first three layers, and then adsorption grows smoothly, since the temperatures used are much higher than the critical temperatures of layering transitions in higher layers. The systems with higher energy of association $u_{as}^*=-2$ and -3 still do not show complete wetting. Again, the attempts to perform Monte Carlo simulations at lower temperatures, of 0.55 and 0.5, and with the starting configura-

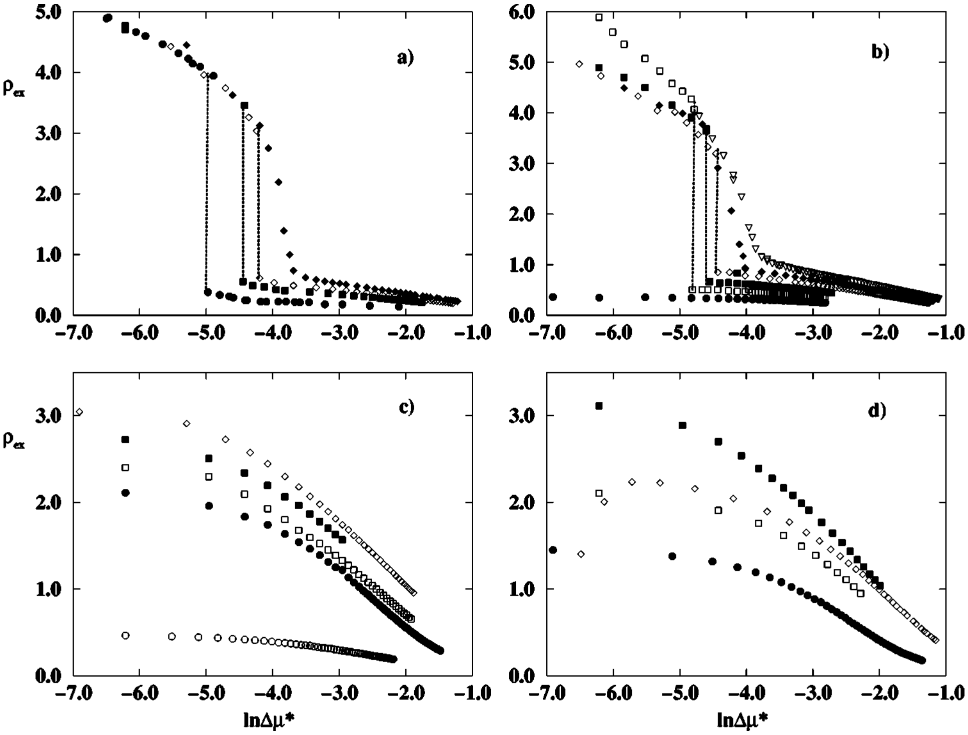

FIG. 6. Adsorption isotherms for the systems with $V_o^* = -0.85$ and different values of the association energy: $u_{as}^* = 0$ (a), -1 (b), -2 (c), and -3 (d). The same symbols correspond to the same temperature in all panels: up triangles, $T^* = 0.6$; open circles, 0.65; filled circles, 0.7; open squares, 0.75; filled squares, 0.8; open diamonds, 0.85; filled diamonds, 0.90; and triangles down, 0.95.

tions corresponding to three, and more, occupied layers, have led to very thin films even at the chemical potentials very close to bulk equilibrium. At still lower temperatures, severe metastability effects do not allow one to obtain any reliable results.

The situation changes considerably for $V_o^* = -0.95$. Although the systems of $u_{as}^* = 0$ and -1 do not show any new behavior, and exhibit the multilayering transition, involving three layers adjacent to the surface. In both cases, the thick films are strongly demixed, as demonstrates Fig. 9. Also, in the case of $u^* = -2$ now new features have been found and the film does not wet the surface at the temperature range down to 0.5. On the other hand, the system of $u_{as}^* = -3$ clearly demonstrates the presence of complete wetting at the temperature $T^* = 0.55$, while at the temperature of 0.6 the adsorbed film is very thin over the entire range of the chemi-

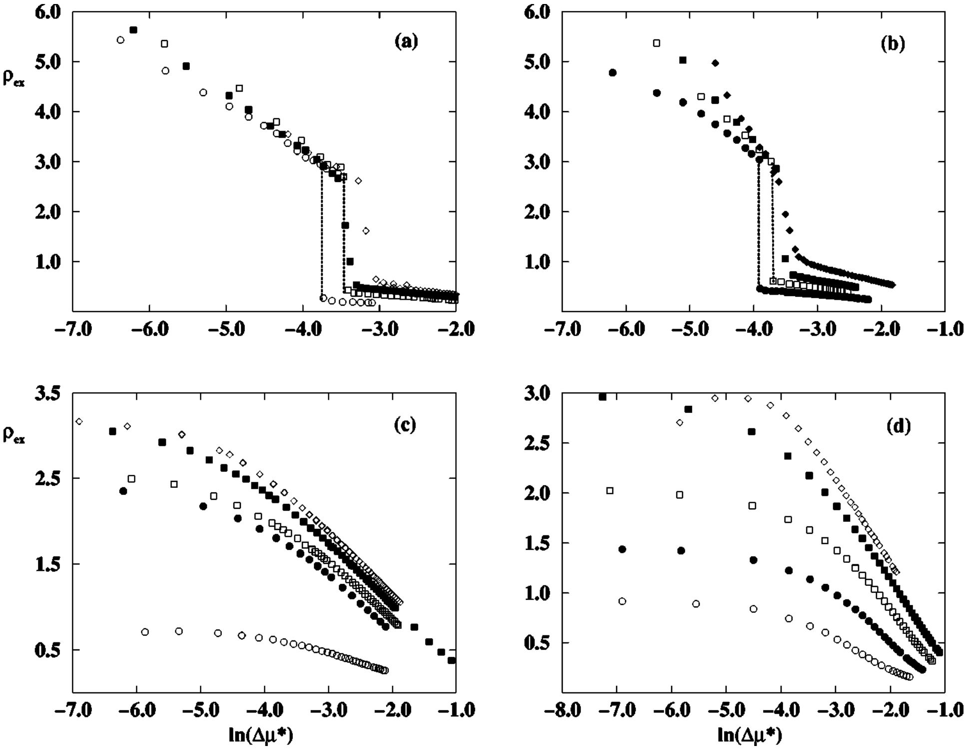

FIG. 7. Adsorption isotherms for the systems with $V_o^* = -0.9$ and different values of the association energy: $u_{as}^* = 0$ (a), -1 (b), -2 (c), and -3 (d). The same symbols correspond to the same temperature in all panels: up triangles, $T^* = 0.6$; open circles, 0.65; filled circles, 0.7; open squares, 0.75; filled squares, 0.8; open diamonds, 0.85; filled diamonds, 0.90; and triangles down, 0.95.

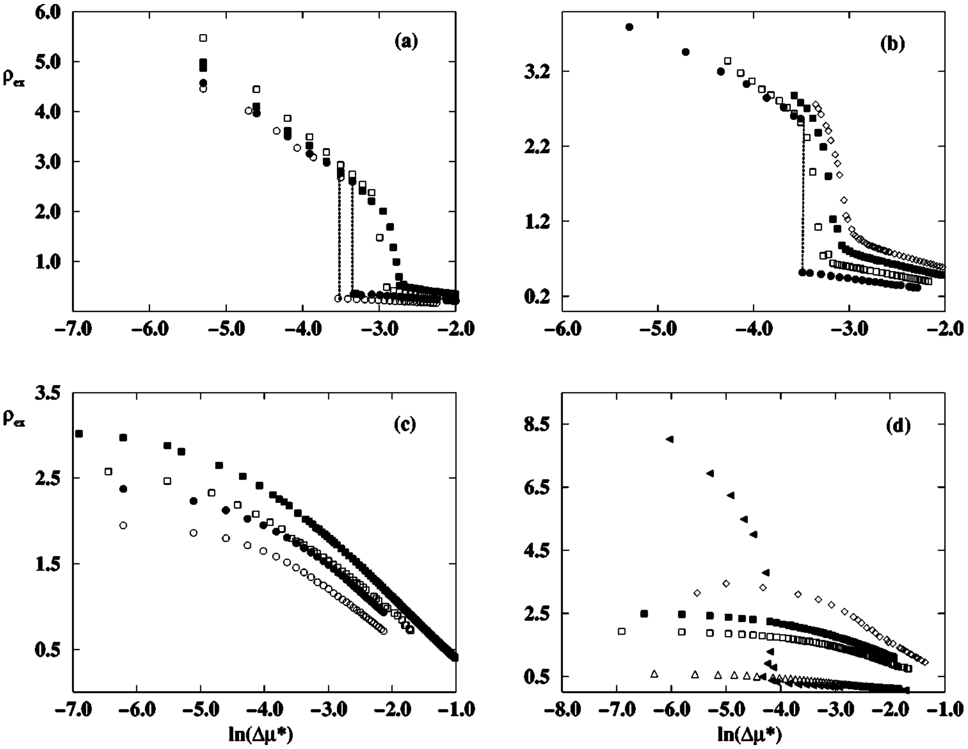

FIG. 8. Adsorption isotherms for the systems with $V_o^*=-0.95$ and different values of the association energy: $u_{as}^*=0$ (a), -1 (b), -2 (c), and -3 (d). The same symbols correspond to the same temperature in all panels: filled triangles left, $T^*=0.55$, up triangles, 0.6; open circles, 0.65; filled circles, 0.7; open squares, 0.75; filled squares, 0.8; open diamonds, 0.85; filled diamonds, 0.90; and down triangles, 0.95.

cal potential. Thus, there must be a dewetting transition, which occurs at the temperature located between $T^*=0.55$ and 0.6. The adsorbed films have equimolar concentration of both components, which are well mixed. At sufficiently low temperatures, the structure of each layer corresponds to the M_2 phase, while at high temperatures, the film is disordered. It is quite well illustrated by the changes of surface excess densities of horizontally and vertically oriented associates against the total surface density, depicted in Fig. 10. The vertically oriented associates show negative surface excess at all temperatures, while the horizontally oriented associates show different behavior at low and high temperatures. Thus, at sufficiently low temperatures the degree of association is rather close to saturation and the surface excess of those associates depends linearly on the total excess density. It is worth noting that the ratio of $\rho_{ex,as}^h/\rho_{ex}\approx 0.5$, since every two adsorbed particles (one of the component *A* and one of the component *B*) form one dimer, as expected for the or-

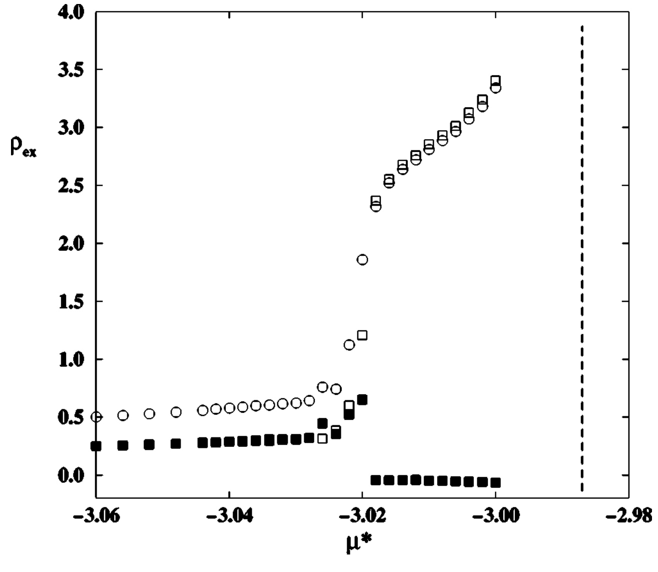

FIG. 9. The adsorption isotherm obtained for the system with $V_o^*=-0.95$ and $u_{as}^*=-1$ at $T^*=0.75$. Circles are for the total surface excess density while open and filled squares represent the surface excess densities of different components. Vertical dashed line marks the location of bulk coexistence.

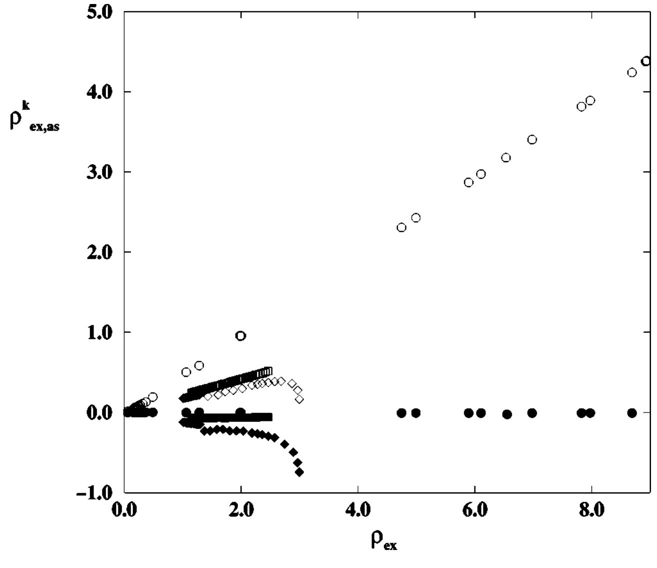

FIG. 10. The surface excesses of horizontally ($k=h$, open symbols) and vertically ($k=v$, filled symbols) oriented associates, $\rho_{ex,as}^k$, versus the total surface excess density, for the system with $V_o^*=-0.95$ and $u_{as}^*=-3$, at different temperatures: $T^*=0.55$, circles; 0.80, squares; and 0.85, diamonds.

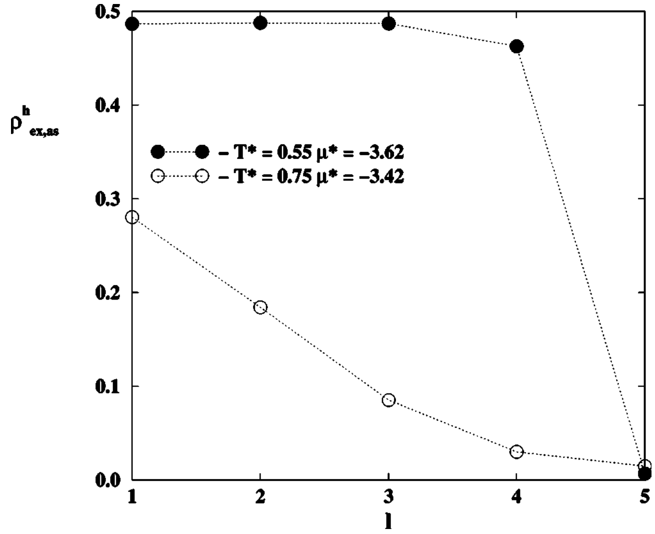

FIG. 11. The density profiles of horizontally oriented associates for the system with $V_o^* = -0.95$ and $u_{as}^* = -3$ at different temperatures (shown in the figure).

dered M_2 phase. At the higher temperature of 0.8, the horizontally oriented associates still change linearly with the total excess density, but the slope of that line is lower, since the film is already disordered and only a fraction of $A-B$ pairs forms dimers. At the highest temperature considered, i.e., $T^* = 0.85$ the surface excesses of the both, horizontally and vertically oriented, dimers drop on approaching bulk coexistence, due to a more rapid increase of the dimers density in the bulk. The formation of the M_2 phase in the adsorbed film is particularly well seen at the density profiles of horizontally oriented associated, shown in Fig. 11. Those profiles have been obtained for the system with $u_{as}^* = -3$ at the temperatures of 0.55 and 0.75 and at the chemical potentials not far from the bulk coexistence.

For the strongest surface field considered, $V_o = -1$, the ground state calculations predict that the first layering transition involves mutual condensation of the first two layers adjacent to the surface, followed by a series of layering transitions, which occur in higher layers. In the case of a single-component adsorption, the critical temperature of the first layering transition is equal to about $T_c^*(1-2) \approx 0.61$ and is considerably higher than the critical temperatures of the layering transitions in higher layers, $T_c^*(l)$, which only slightly exceed the critical temperature of a strictly two-dimensional system, equal to $T_{c,1}^* = 0.5673$ [26], and converge to the roughening temperature T_R as $l \rightarrow \infty$ [26]. In the case of binary mixtures characterized by the energy of association u_{as}^* between 0 and -3, the situation is similar, as predicted by the ground state considerations. Figure 12 presents the examples of adsorption isotherms calculated for the systems with different u_{as}^*. In the case of $u_{as}^* = 0$ and -1 [see Figs. 12(a) and 12(b)] the situation is just as described. In particular, we find the layering transition involving mutual condensation in layers 1 and 2. In both cases the film is strongly demixed.

In the case of $u_{as}^* = -2$ we have found a clear evidence of layering transitions and complete wetting at a very low temperature of 0.4 [see Fig. 12(c)]. In particular, apart from the first layering, which involves the condensation in the first two layers, the formation of the third layer also occurs via the first-order transition. Although the subsequent layers appear to grow continuously, there are rather large technical problems due to proximity of the bulk coexistence and the

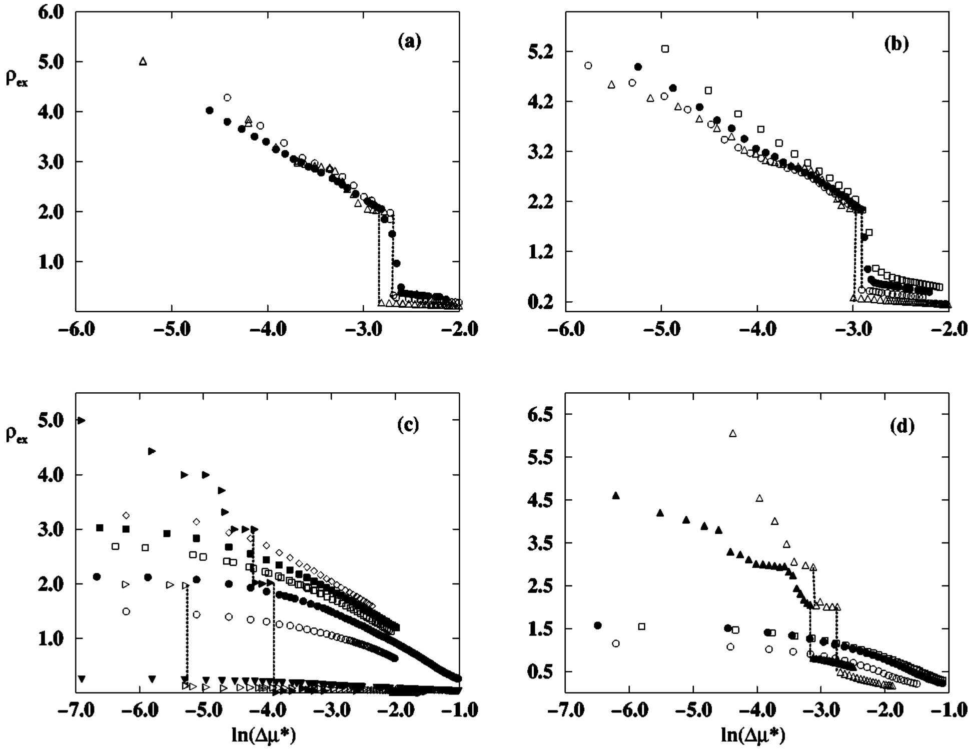

FIG. 12. Adsorption isotherms for the systems with $V_o^* = -1.0$ and different values of the association energy: $u_{as}^* = 0$ (a), -1 (b), -2 (c), and -3 (d). The same symbols correspond to the same temperature in all panels: filled triangle right, $T^* = 0.40$; open triangle right, 0.50; filled down triangle, 0.55; up triangles, 0.6; filled triangle up, 0.64; open circles, 0.65; filled circles, 0.7; open squares, 0.75; filled squares, 0.8, open diamonds, 0.85; filled diamonds, 0.90; and down triangles, 0.95.

results are rather noisy. The results obtained at the temperature equal to 0.5 require some comments. The adsorption runs have led only to the formation of a bilayer on approaching bulk condensation. Therefore, it is quite possible that the film does not wet the surface at that temperature. We have also attempted to start the desorption runs very close to the bulk condensation point and using the starting configuration with three as well as four occupied layers. However, the system always relaxed to the configuration with only two filled layers.

For $u_{as}^{*}=-3$ the layering also occurs at sufficiently low temperatures, below 0.64. As soon as the temperature exceeds that threshold value, the adsorption isotherms do not show any trace of layering transitions as well as wetting. We have performed the simulation starting at the chemical potential very close to bulk coexistence and with the starting configuration consisting of various numbers of occupied layers, and found that after equilibration the system always relaxes to the low density state. Thus, the results provide a rather strong evidence of dewetting transition at the temperature of about 0.64.

V. SUMMARY AND FINAL REMARKS

We have performed extensive Monte Carlo simulations for adsorption of associating symmetric binary mixtures at attractive walls. Our study has aimed at the determination of the interplay between the effects of molecular association and the wetting of the substrate by the mixture. Using the lattice gas formalism we have selected a series of systems characterized by different values of the association anergy and by different strength of the surface potential, taken to be same for both components. In particular, the values of the association energy have been chosen in such a way that the bulk phase is always demixed ($u_{as}^{*}\geqslant-1$) or it exhibits mixing over a certain range of the temperature and the chemical potentials of both components ($u_{as}^{*}<-1$). The simulations have been carried out along the path of equal chemical potentials for both species.

The results obtained have demonstrated that the wetting behavior of the mixtures studied depends strongly on the effects of association, which take place in the adsorbed film as well as in the bulk. In particular, when the systems exhibit nonzero wetting temperature, the increase of association energy leads to the increase of the wetting temperature. Since the increasing effects of association reduce the temperature range over which the dilute gas phase exists, the adsorption systems with high values of u_{as}^{*} do not show complete wetting at all. The system characterized by $u_{as}^{*}=-2$ is particularly interesting, due to rather peculiar behavior of the bulk. Gradual demixing of the condensed phase occurs over a certain interval of temperatures, between T_1^{*} and T_2^{*}, such that below for $T^{*}<T_1^{*}$ the bulk liquid is mixed, while at $T^{*}>T_2^{*}$ it is demixed. These quite different thermodynamic conditions at bulk coexistence influence the behavior of adsorbed films. The adsorbed layer exhibits complete mixing, even at the temperatures exceeding T_2^{*}. Thus, at the coexistence the mixed thick film must undergo demixing transition, when the macroscopically thick liquid layer is formed. There, probably, exists a certain free energy barrier for that demixing transition and hence the development of thick (mixed) wetting layers is seriously hindered.

The most interesting finding of this work concerns the evidence of dewetting transition, which occurs upon the increase of temperature in the systems characterized by sufficiently high energy of association. The dewetting temperature increases with the increase of the strength of the surface potential. The mechanism, which leads to that behavior, is not quite clear, however. In general, it cannot be attributed to the above discussed temperature changes of the bulk liquid structure, which have been found for $u_{as}^{*}=-2$, but do not take place when the association energy is higher, e.g., $u_{as}^{*}=-3.0$. Besides, the temperatures at which the dewetting, for $u_{as}^{*}=-2$, occurs are considerably lower than the temperature at which the demixing of the bulk phase begins (T_1^{*}). A more systematic study of the changes of dewetting temperature on the strength of the surface field and the magnitude of the association energy are needed to determine the mechanism of dewetting transition.

Another interesting question concerns the formation of adsorbed layers on surfaces characterized by a stronger surface potential, when the film growth occurs via a sequence of layering transitions. It is possible that even such systems may exhibit incomplete wetting and the layering transitions may terminate at a finite thickness of the film, when the association energy is high enough.

Other classes of systems that would also require study involve symmetric as well as nonsymmetric associating binary mixtures in contact with selective walls. In such cases, the association of the molecules adsorbed is expected to lead to a quite different structure of surface layers. When the interactions of both components with a wall are different, the dimers may be more likely to assume orientation perpendicular to the surface and this may also influence wetting behavior. Besides, in order to fully understand the phase behavior of nonuniform associating mixtures, it would be also desirable to use different thermodynamic conditions, regarding the relation between the chemical potentials of both species. In our earlier study of nonassociating nonuniform binary mixtures [9–11] it was clearly demonstrated that their phase behavior is very complex and in several aspects has no counterparts in simple one-component systems. Molecular association is expected to add still new elements to the phase behavior of adsorbed layers.

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