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Computer simulation of phase diagrams of trimers adsorbed on a square lattice

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Monte Carlo simulations in the grand canonical ensemble, the histogram reweighting technique, and finite-size scaling are used to study the phase behavior of monolayer films formed by various trimers on a square lattice. The multisite occupancy model is considered. The molecule is assumed to be a chain composed of segments *A* and *B*. The bonds between segments cannot be broken. We discuss three types of chains: *BBB*, *ABB*, and *BAB*. In all cases we analyze the behavior of molecules that have different shapes, namely, linear and L-shaped rigid rods and flexible trimers. The presented investigation shows that the chemical structure and geometrical shape of molecules can radically alter the phase diagram topology. The stable ordered structures have been found for some types of trimers. The structural transitions between disordered fluid and ordered fluid have been observed. The results reveal a great variety of vapor-liquid coexistence behavior depending on shapes of molecules and their chemical structure.

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I. INTRODUCTION

A knowledge of coexistence properties of thin surface films is essential for many practical applications. Therefore, there have been significant theoretical and experimental efforts toward the determination of phase diagrams for single-component adsorbed monolayers.[1,2]

The relation between a model of the system and its phase behavior is a fundamental problems in modern physics. The determination of complete phase diagrams corresponding to a given model is a very demanding task. There is only a handful of exact analytical solutions obtained for significant but rather exceptional cases. For most models, the phase diagrams cannot be calculated exactly and rather crude approximations have to be used. In two-dimensional (2D) geometry of adsorbed layers, statistical fluctuations play a much more important role than in 3D systems, so simple approximations, such as various variants of mean-field theory, give inaccurate results. However, in recent years molecular simulations have become an effective tool to generate phase diagrams even for complex fluids.

Models used in such investigations involve two fundamental elements: an architecture of molecules and intermolecular potentials. In the simple models a molecule is assumed to be a point source of intermolecular potential. For molecules without internal degrees of freedom the relation between the potential and phase behaviors of the fluid is well known. The category of phase diagrams is largely determined by the range and strength of attractive and repulsive interactions.[3–6] A very interesting fact is the presence of liquid polymorphism in simple fluids. In addition to the usual vapor-liquid transition certain fluids may exhibit double criticality with a second liquid-liquid critical point.[7] The double criticality was found for the density-dependent pair potential.[7]

Phase behavior of fluids with embedded anisotropic features such as electric or magnetic moments is more complicated. Various classes of molecules having internal degrees of freedom were considered, for instance, Heisenberg spin fluid,[8–10] a dipolar fluid,[11,12] and the van der Waals–Potts fluid.[13] The most interesting results emerged from the interplay between internal and translational degrees of freedom. These interrelations lead to unusually rich phase diagram topologies.

In another class of fluid models a molecule is treated as a chain of the same or different units linked together. Intermolecular forces are described by the multicenter potential. The simplest molecule of this kind is a dimer. For many years systems involving dimers have been studied in the framework of lattice-based and continuum fluid models.[14–28] The key problem in multisite occupancy lattice models is to compute a number of possible configurations. Contrary to the usual single-site problem, there is no statistical equivalence between particles and vacancies. Occupation of a given site implies that at least one neighbor site is also occupied. Results connected with dimer statistics have been reported by Fowler and Rushbrooke[14] and Flory.[15] More recently, a large number of studies has dealt with two-dimensional layers consisting of homonuclear dimers.[16–23] One of the most interesting problems is structural ordering and phase transitions in monolayers. Phares *et al.*[23] have proved, using the transfer-matrix method, that there was a finite number of ordered structures for repulsive nearest-neighbor interactions between dimers. Monolayer films of homonuclear dimers have been intensively studied by means of Monte Carlo simulations. Adsorption on square,[24] triangular, and honeycomb[25] lattices was considered for repulsive and attractive interactions between dimers. An influence of energetical heterogeneity of the surface on phase transitions and critical behavior of attracting dimers has been also analyzed.[26] These studies have shown that monolayers of homonuclear dimers belong to the 2D Ising class of universality.

It is of interest to study phase behavior of dimers consisting of different segments *A* and *B*. Monte Carlo simulations have been recently carried out for some model fluids.[27] The results reveal a surprisingly great variety of vapor-liquid coexistence behaviors depending on the relative strengths of interactions between molecule segments. Apart from the usual vapor-liquid coexistence, a second phase transition between the disordered and ordered liquid was found. The majority of systems consisting of heteronuclear dimers belong to the 2D Ising class of universality. However, in the case of repulsive *A-A* coupling and attractive interactions of *B-B* and *A-B* types the fluid exhibits a nonuniversal behavior.[28] One sees that the chemical structure of fluid molecules strongly affects phase transitions and critical properties of one-component fluids.

The recent development of simulation techniques makes it possible to perform phase equilibrium calculations for long chains. Because knowledge of phase behavior of alkane systems is important for the petrochemical industry, a large number of simulations has been performed for normal and branched alkanes. In the usually used representations the groups CH_3, CH_2 or CH are described by single interaction sites.[29] Many different models have been proposed to describe interactions between alkanes.[29–39] Various force fields have been used to determine coexistence curves with a very good accuracy.[38–41] The calculations were carried out for three-dimensional continuous-space models.

It is quite obvious that a dimensionality of the system largely affects its phase behavior. However, to our best knowledge, the vapor-liquid coexistence in two-dimensional layers of long molecules has not been intensively studied. At this point in time, it is unclear which elements of the microscopic structure of molecules decide the nature of phase transitions in the system. In such a situation, trimers seem to be very good model particles to study the influence of the geometrical shape and chemical structure of molecules on the vapor-liquid coexistence. We investigate the behavior of rodlike and flexible chains. The rigid rods can be linear or L-shaped. Moreover, we can consider trimers composed of the same or different segments. The relatively short trimers can adsorb parallell to the surface, so the existence of two-dimensional films is quite probable. Knowledge of the way in which phase diagrams of trimers depend on their molecular shapes can be important in understanding the vapor-liquid coexistence in real systems.

In this paper we analyze phase transitions in one-component fluids consisting of trimers. The main purpose of this work is to show how the chemical structure and geometrical shapes of molecules affect the vapor-liquid equilibrium.

The structure of the paper is as follows: in Secs. II and III we describe the model and the simulational procedures, whereas in Sec. IV the results of calculations are discussed. We close in Sec. V with a summary and conclusions.

II. MODEL

We consider a square lattice in two dimensions consisting of L^2 sites. A lattice site is occupied by one segment or is empty. A molecule is a trimer composed of segments *A* and *B*. The bonds between segments cannot be broken. We consider three types of chains: *BBB*, *ABB*, and *BAB*. In all cases we analyze behavior of molecules of different shapes, namely, linear and L-shaped rigid rods and flexible trimers. The energies of nearest-neighbor interactions between segments belonging to different molecules are u_{AA}, u_{AB}, and u_{BB}. The relations between these parameters dictate the thermodynamical properties of the fluid. There are many different sets of the interaction parameters (u_{AA}, u_{BB}, u_{AB}). In this work we carry out simulations for a special class of trimers for which $u_{AA}=u_{BB}=-1$ and $u_{AB}=0$.

Let us introduce the occupation variables cx_i [x denotes the type of atom (A or B)], which can take the values $cx_i=1$, when a site is occupied by atom x, and $cx_i=0$, when unoccupied. Thus, each lattice site is characterized by a pair of occupation variables (cA_i, cB_i). In the grand canonical ensemble the Hamiltonian of N trimers at a given temperature T can be written as

$$H=u_{AA}\sum_{\langle i,j\rangle} cA_icA_j+u_{BB}\sum_{\langle i,j\rangle} cB_icB_j+u_{AB}\sum_{\langle i,j\rangle} cA_icB_j -Nu^*-N\mu, \tag{1}$$

where μ denotes the chemical potential of dimers and u^* is the energy of interactions between segments belonging to the same molecule: $u^*=2u_{BB}$ for *BBB*, $u_{BB}+u_{AB}$ for *ABB*, and $2u_{AB}$ for *BAB*. The sums are over all pairs of nearest-neighbor lattice sites. Because we have taken into account interaction energies of all possible pairs of segments we subtract the term (Nu^*). The Hamiltonian (1) describes the multisite occupancy lattice model in which a molecule is treated as a source of the three-centered, short-range potential of intermolecular interactions. We employ dimensionless units, i.e., energies are given in units $|u_{BB}|$, temperatures in units $|u_{BB}/k_B|$, and lengths in units of the lattice constant.

III. MONTE CARLO PROCEDURES

We describe here only the most significant aspects of the method. For detailed accounts of the simulation techniques, readers are referred to the reviews and original works.[42–47] All simulations were conducted in the grand canonical ensemble using hyper-parallel tempering.[45] The square simulation cell was used with the standard boundary conditions in both directions. The linear size of the system L ranged from 24 to 72. The Monte Carlo step consisted of an attempt to insert a trimer molecule at a randomly chosen position or an attempt to remove an existing particle. The equilibrium states were reached after discarding 10^5-10^7 Monte Carlo steps (MCS) (per site). The averages were calculated over next 10^7 MCS. To avoid correlations between subsequently generated states, sampling to evaluate the averages was carried out at intervals of 200 MCS. We have calculated $\rho=\langle c\rangle/L^2$, where $\langle c\rangle$ denotes the average number of occupied lattice sites and the average energy $\langle u\rangle$.

The multiple-histogram reweighting was applied to estimate phase diagrams. The coexistence curves were determined according to a ‘‘two-state approximation’’ from the density distribution[46]

$$p(\rho)=\sum_u P(\rho,u), \tag{2}$$

where $P(\rho,u)$ is the two-dimensional histogram. In the case of a first-order transition the density distribution $p(\rho)$ had a

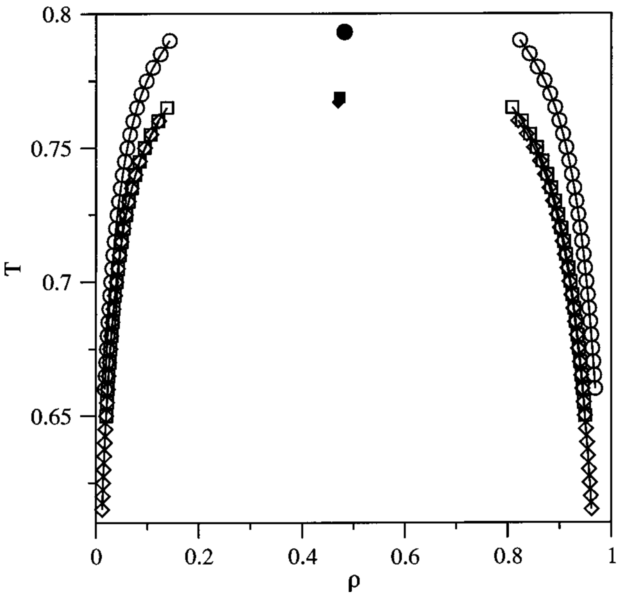

FIG. 1. Phase diagrams in the T-ρ plane for various homogeneous trimers: rodlike linear (circles), rodlike L shaped (squares), and flexible (diamonds).

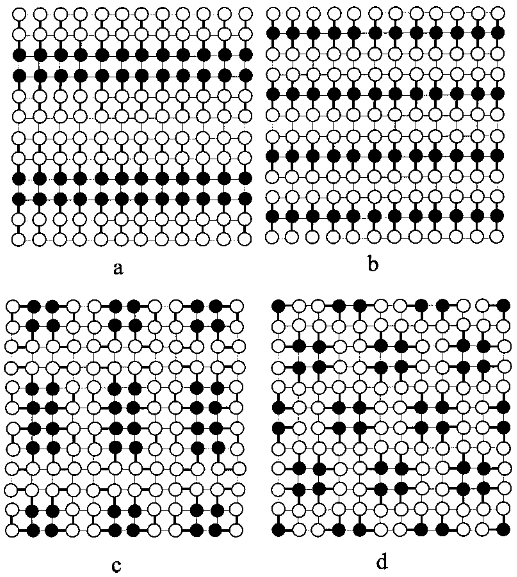

FIG. 2. The ordered structures for the rodlike heterogeneous trimers: (a) linear *ABB*, (b) linear *BAB*, (c) L-shaped *ABB*, and (d) L-shaped *BAB*.

double peaked structure. The location of a coexistence point had been achieved by tuning the chemical potential at a given temperature until the areas under both peaks became the same.

A critical behavior of the system was studied using finite scaling procedures. The fourth-order cumulant of the order parameter was calculated as[47]

$$U_L = 1 - \langle m^4 \rangle_L / 3 \langle m^2 \rangle_L^2, \tag{3}$$

where $m = \rho - \langle \rho \rangle$ and $\langle m \rangle_L$ denotes the average evaluated for the system of the size L. The cumulants adopted a nontrivial universal value U^* at the critical point, irrespective of system sizes L. Thus, plotting functions $U_L(T)$ for different L yielded an insertion point $U(T_c) = U^*$, which gives an accurace estimate of the critical temperature in the infinite system. The results are discussed in the next sections.

IV. RESULTS AND DISCUSSION

A. Homogeneous trimers

It is interesting to show how vapor-liquid coexistence properties depend on the shape of molecules. Figure 1 presents phase diagrams for three kinds of homogeneous trimers *BBB*: linear and L-shaped rodlike molecules and flexible chains. The solid lines are provided as a guide to the eye for the simulation data.

It is evident from these results that the shape of molecules considerably affects phase behavior of the fluid. The coexistence curve T vs ρ for the L-shaped trimers lies below the curve for linear molecules. However, flexible trimers exhibit almost the same phase behavior as the L-shaped rods. The similar relation between coexistence curves for linear and more complex molecules has been found in the case of *n*-alkanes and their branched isomers.[41] To complete the coexistence curves we found the critical points. We used the standard finite scaling procedure of Binder.[47] All considered fluids consisting of homogeneous trimers belong to the 2D Ising class of universality. The estimated critical temperatures are as follows: 0.7932 (linear rodlike trimers), 0.7687 (L-shaped rodlike trimers), and 0.7670 (flexible trimers). It seems to be instructive to mention that the critical temperatures for monomers and dimers are equal to 0.567 25 and 0.689, respectively.[24]

B. Heterogeneous trimers

As has been already mentioned the heteronuclear dimers exhibit a rich vapor-liquid behavior depending on values of model parameters.[27] In addition to gas-liquid coexistence, heterogeneous dimers can exhibit the transition between disordered fluid and ordered fluid. The vapor-liquid coexistence is influenced by the proximity of the structural transition. Similar effects were reported for numerous, quite distinct models, such as spin fluid,[48] dipolar fluids,[11,12] and symmetrical binary fluid mixtures.[49] In these systems, apart from vapor-liquid coexistence, one can observe other transitions, for example, paramagnetic-ferromagnetic or mixed fluid–demixed fluid. The latter transitions are connected with differences in internal properties of molecules. Each particle carries an internal degree of freedom, or it is a concrete chemical compound. However, the heterogeneous dimer can be differently oriented relative to surrounding molecules. The critical temperature of such a transition depends on the density. Consequently, in the space T-ρ we obtain a critical line that is usually called a "λ line."[48,50] One can distinguish three categories of phase diagrams depending on the path of the λ line relative to the vapor-liquid coexistence envelope.[49] In the first type of diagrams the λ line approaches the vapor-liquid phase boundary well below the vapor-liquid critical point. The λ line intersects the vapor-liquid line at the so-

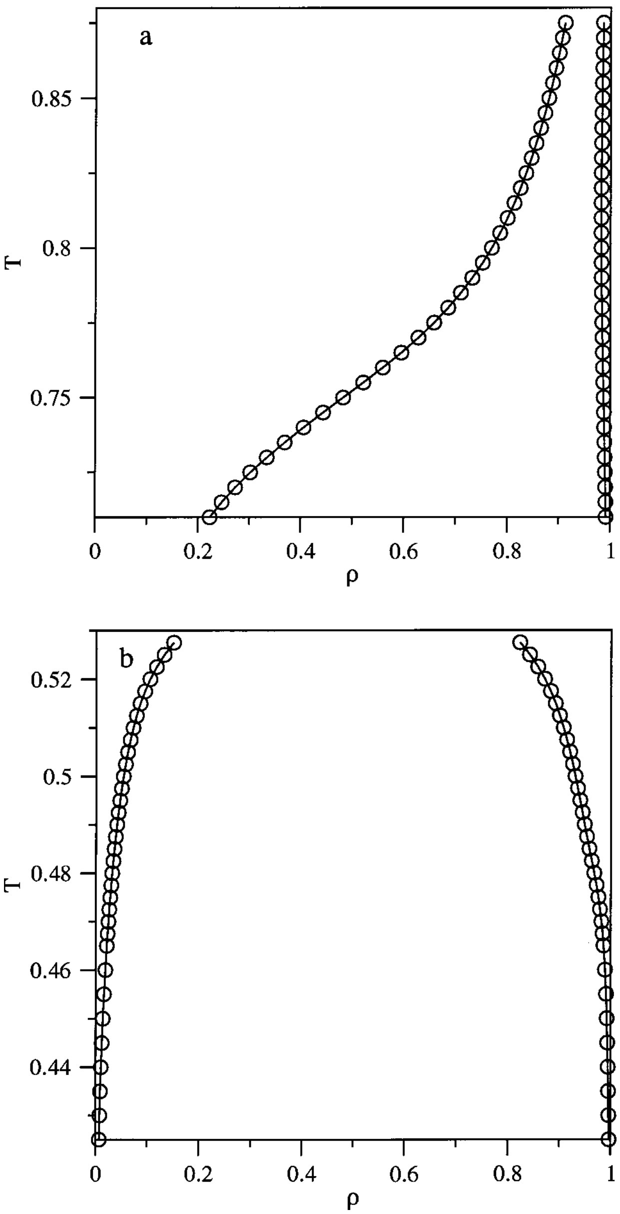

FIG. 3. Phase diagrams for the *ABB* trimers: (a) linear and (b) L shaped.

called critical end point. There is only one first-order transition in the system. However, the diagrams of the second type correspond to a situation in which two first-order transitions occur in the system, so double criticality and triple-point behavior is observed. The λ line can approach the vapor-liquid line close the vapor-liquid critical point. For the third category of phase diagrams the λ line intersects the vapor-liquid line just at the vapor-liquid critical point.[48] In the case of heteronuclear dimers, phase diagrams belonging to the second class have been found. One can see a point where a vapor coexists with two phases, namely, a disordered liquid having intermediate density and the dense ordered liquid.[27] In this study we address the question of the effects of the chemical structure and geometry of trimers on the phase diagram topology.

Depending of chemical structure and the shape of molecules the Hamiltonian (1) has different ground states at full coverage. These are indicated in Fig. 2. For all studied molecules contacts between *A* and *B* segments are energetically nonprofitable so configurations without these contacts are strongly preferred. In the case of rigid linear trimers *ABB* and *BAB* such a configuration corresponds to the alternating *A* and *B* rows oriented in *x* or *y* directions [Figs. 2(a) and 2(b)]. For the L-shaped trimers *BAB* the periodic ordered structures without *AB* pairs are more complicated [Fig. 2(d)]. However, there is not such a favorably ordered structure for the L-shaped molecules *ABB*. The pairs *AB* always exist in such close-packed monolayers [Fig. 2(c)]. As will be shown below, the orientational order in the system is responsible for the special type of phase diagrams.

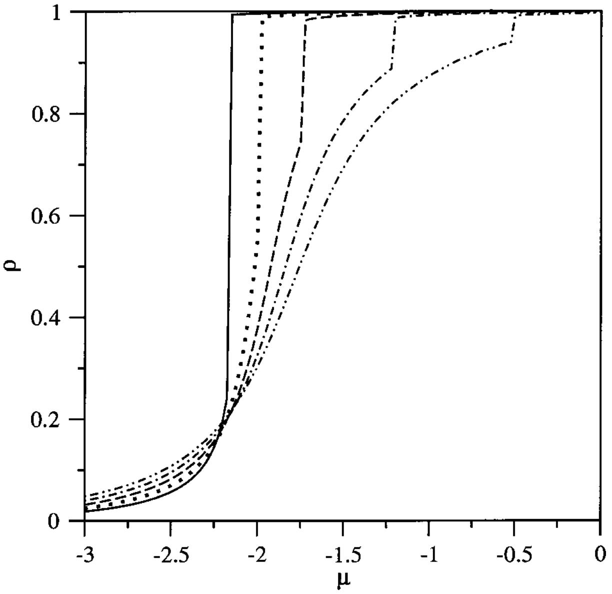

FIG. 4. Adsorption isotherms for the *ABB* trimers at different temperatures: 0.7 (solid line), 0.75 (dotted line), 0.8 (dashed line), 0.85 (dot-dashed line), and 0.9 (dot-dot-dashed line).

First, we would like to discuss the results obtained for rodlike molecules. In Fig. 3 the phase diagrams for linear and bent rods *ABB* are presented. The coexistence curve for the linear molecules is highly asymmetric, having an unusual shape in the form of a "swan neck." A similar coexistence envelope has been found for shorter linear molecules, i.e., for dimers *AB*.[27] Obviously, coexistence temperatures for dimers were less than those for trimers. It may be instructive to show the examples of isotherms that have been used to estimate the phase diagram. In Fig. 4 one can see that at low temperatures, in the isotherm a high vertical step appears, corresponding to condensation. For higher temperatures the condensation jump is less pronounced and shifted to high densities. It is very interesting that the phase diagram for the L-shaped molecules *ABB* [Fig. 3(b)] is completely different and quite similar to those obtained for homonuclear trimers (see Fig. 1). Moreover, in this case the coexistence temperature at a given density is considerably lower than that for linear molecules.

To understand the difference in phase behavior of the geometrical isomers it is useful to investigate the structure of

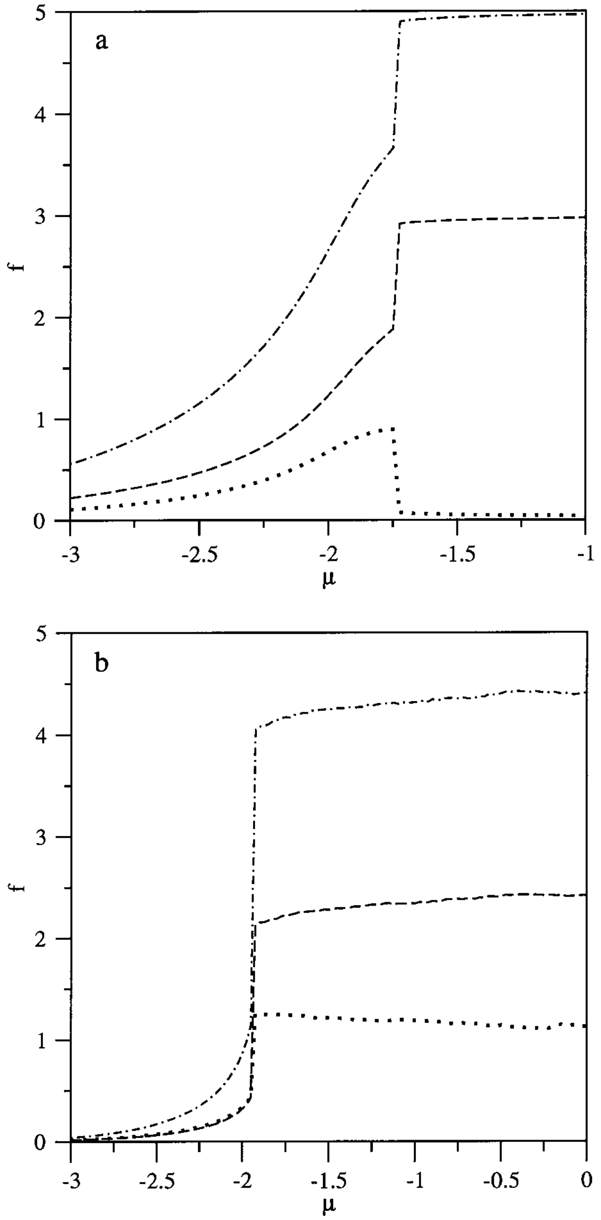

FIG. 5. Dependencies of the structure parameters on the chemical potential f_{BB} (dot-dashed lines), f_{AA} (dashed lines), and f_{AB} (dotted lines) for the rodlike *ABB* trimers: (a) linear, $T=0.8$ and (b) L shaped; $T=0.5$.

dense phases formed by both kinds of trimers. To this end we define the structure parameter $f_{\alpha\beta}$,

$$f_{\alpha\beta}=\langle n_{\alpha\beta}\rangle/\langle N\rangle, \tag{4}$$

where $\langle n_{\alpha\beta}\rangle$ is an average number of nearest-neighbor pairs $\alpha\beta$ (α, $\beta=A$ or B) and $\langle N\rangle$ is an average number of trimers. Each trimer has eight possible "contacts" so the structure parameter (4) ranges from 0 to their maximum values: $f_{AB}=8$, $f_{AA}=3$, and $f_{BB}=5$ for the *ABB* trimers and $f_{AB}=8$, $f_{AA}=2$, and $f_{BB}=6$ for *BAB* trimers.

Figure 5 shows the dependencies of the structure parameters on the chemical potential for isomeric rodlike trimers *ABB*. In both cases, the structure parameters are close to zero for low densities, they increase until the condensation point is achieved, and then they jump abruptly. After the vapor-liquid transition we observe a different behavior of the linear and L-shaped trimers. In the case of linear molecules the structure parameters f_{AA} and f_{BB} reach their maximum values, whereas a number of *AB* contacts is close to zero. It means that the dense phase is almost completely ordered even for relatively high temperatures. The entropy of the liquid is very low. However, in the fluid consisting of the bent trimers, the structure parameters do not achieve their extreme values, i.e., the dense phase is disordered and has rather high entropy. The occurrence of spontaneous orientational ordering of linear molecules and a lack of a similar ordering in the L-shaped trimers explain the difference in the phase diagram topology. In the case of linear molecules there is a transition between a disordered gas and the ordered liquid, whereas for the L-shaped trimers both gas and liquid are disordered. It is clear that the entropy effects play an essential role in the phase behavior of isomeric rigid rods. It is also worth noting that the occurrence of ordered structures in the liquid causes an increase of the coexistence temperatures.

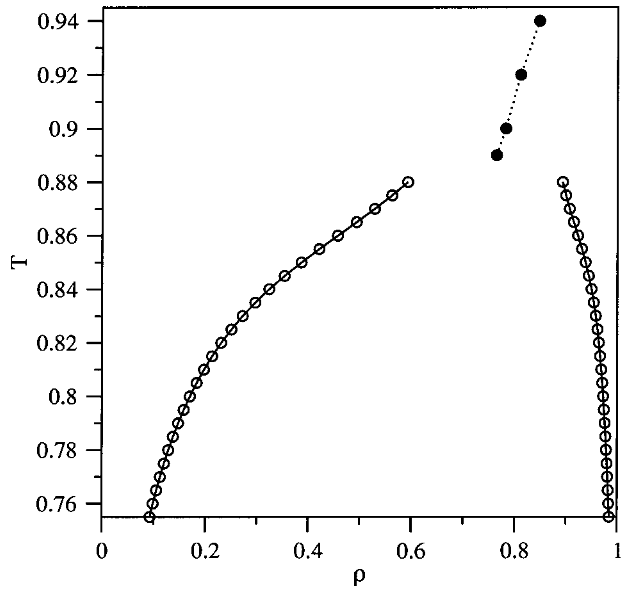

FIG. 6. The phase diagram for the rodlike linear *BAB* trimers.

We would like to show how the chemical structure of trimers affects their vapor-liquid equilibria. To this end we performed calculations for the trimers *BAB*. The phase diagram has been estimated only for the linear trimers. However, for the L-shaped molecules preliminary simulations were carried out for selected temperatures.

Comparing the coexistence curves for linear rigid rods *ABB* [Fig. 3(a)] and *BAB* (Fig. 6) one sees that the position of the noninteracting segment *A* in the chain is important in determining physical properties of the fluid. In the case of *BAB* trimers, the phase diagram is not as drastically asymmetric as for the molecules *ABB*. The gas branch of the diagram lies higher than that for the *ABB* trimers, and the critical point is shifted to the middle value $\rho=0.5$. Figure 7(a) presents examples of isotherms for the *BAB* trimers. Notice

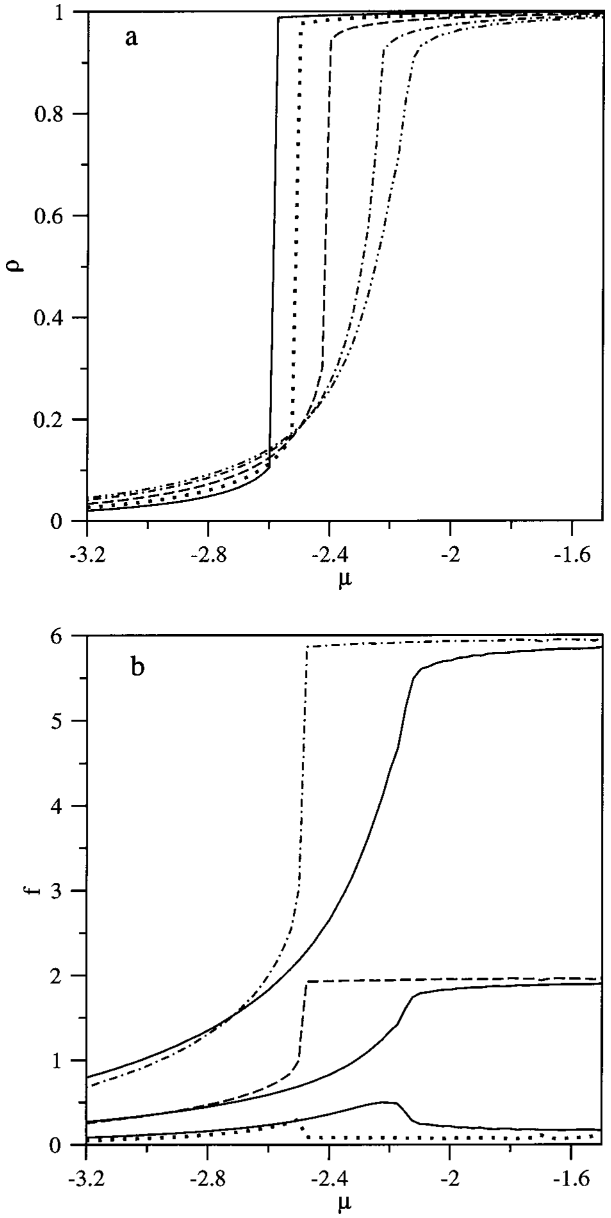

FIG. 7. Adsorption isotherms (a) and structure parameters (b) for the rodlike linear *BAB* trimers. (a) provides values at the following temperatures: 0.75 (solid line), 0.8 (dotted line), 0.85 (dashed line), 0.9 (dot-dashed line), and 0.925 (dot-dot-dashed line); (b) f_{BB} (dot-dashed line), f_{AA} (dashed line), and f_{AB} (dotted line) at $T = 0.8$ and 0.925 (solid lines).

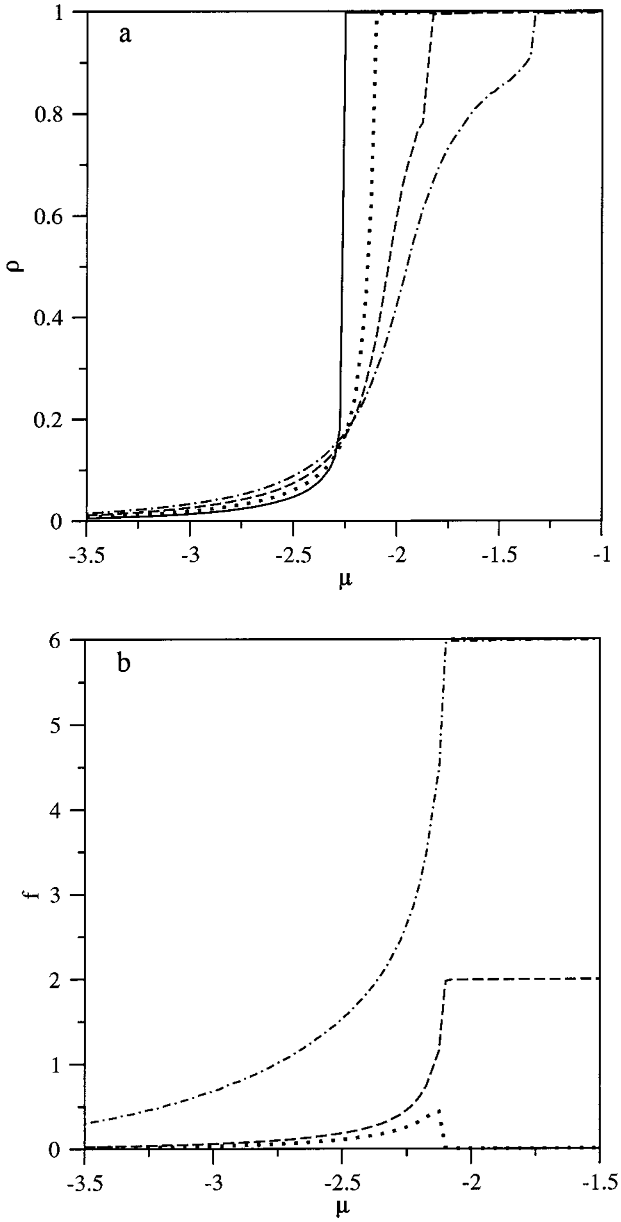

FIG. 8. Adsorption isotherms (a) and structure parameters (b) for the rodlike L-shaped *BAB* trimers. (a) provides values at the following temperatures: 0.65 (solid line), 0.7 (dotted line), 0.75 (dashed line), and 0.8 (dot-dashed line); (b) f_{BB} (dot-dashed line), f_{AA} (dashed line), and f_{AB} (dotted line); $T = 0.7$.

that the isotherms at $T = 0.9$ and 0.925 are continuous. In Fig. 7(b) we show the dependencies $f_{\alpha\beta}$ vs μ at two temperatures: below ($T = 0.8$) and above ($T = 0.925$) the vapor-liquid critical temperature. In both cases, for sufficiently high values of the chemical potential the system achieves complete ordering in the dense phase. At lower temperature one sees a sharp change in the degree of ordering. However, at $T = 0.925$ the transition between disordered fluid and ordered fluid is continuous. We observe the second-order structural transition even for high temperatures. The measured locus of the λ line for this transition is shown in Fig. 6. We suppose that the phase diagram exhibits the tricritical-point topology. The tricritical point (T_t) is located in the interval 0.86–0.88. A precise location of the tricritical point is beyond of the scope of the present study.

Now, we would like to analyze a series of isotherms calculated for the L-shaped trimers *BAB* [Fig. 8(a)]. One notices that these isotherms are very similar to those for linear *ABB* trimers (see Fig. 4), i.e., at all temperatures the liquid density is close to unity, and small condensation steps are observed at high values of the chemical potential. One can easily imagine a hypothetical phase diagram for the L-shaped trimers. It is likely analogous to that for the linear *ABB* trimers. This somewhat surprising observation is quite clear in the light of analysis of orientational ordering of the liquid [Fig.

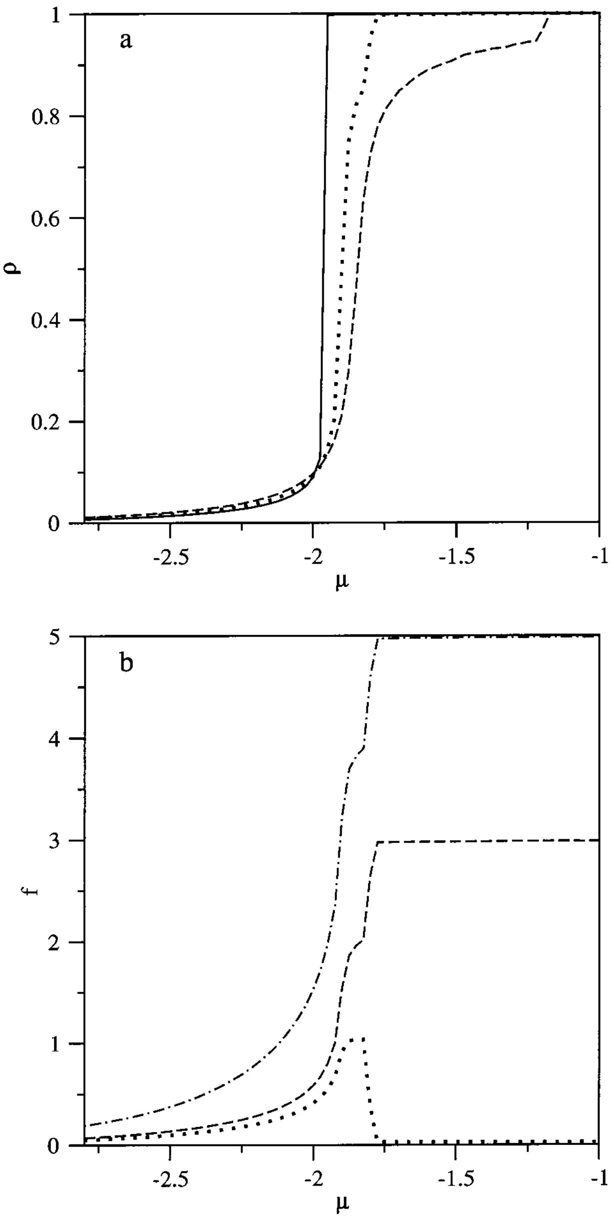

FIG. 9. Adsorption isotherms (a) and structure parameters (b) for the flexible *ABB* trimers. (a) provides values at the following temperatures: 0.55 (solid line), 0.575 (dotted line), and 0.6 (dashed line); (b) f_{BB} (dot-dashed line), f_{AA} (dashed line), and f_{AB} (dotted line); $T=0.575$.

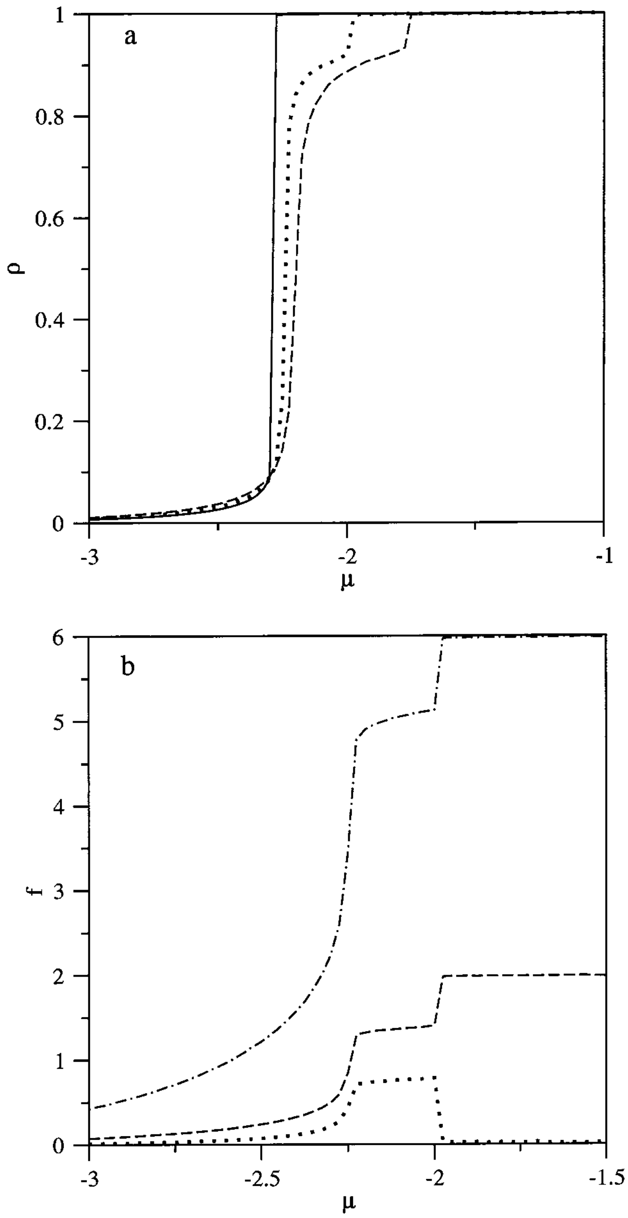

FIG. 10. Adsorption isotherms (a) and structure parameters (b) for the flexible *BAB* trimers. (a) provides values at the following temperatures: 0.575 (solid line), 0.6 (dotted line), and 0.625 (dashed line); (b) f_{BB} (dot-dashed line), f_{AA} (dashed line), and f_{AB} (dotted line); $T=0.6$.

8(b)]. As for the linear molecules *ABB* in the dense phase the structure parameters achieve their extreme values. Therefore, we can suppose that there is a transition between a disordered gas and the ordered liquid [see Fig. 2(d)].

The next important problem is the role of molecular flexibility in phase equilibria. We carried out simulations for the flexible trimers *ABB* and *BAB*. Examples of isotherms and structure parameters are shown in Figs. 9 and 10. One can find an analogy between behavior of the flexible and linear rigid rods of the *ABB* type. At low temperatures isotherms have sharp jumps to unity, and on increasing temperature the steps move to high values of chemical potential and become small. Moreover, it is evident that the liquid exhibits a high degree of ordering. Therefore, one can expect that the phase diagram for flexible molecules *ABB* is of a similar type as that estimated for the linear rigid trimer [Fig. 3(a)]. In the case of *BAB* chains the behavior of flexible molecules may be to some degree similar to the L-shaped rigid rods. In general, the flexible molecules tend to an energetically stable structure if such a configuration exists in the system.

Two steps are observed on the curves $f_{\alpha\beta}$ vs μ; the first is smooth, whereas the other is a discontinuous one. The latter corresponds to a vertical step at the isotherm. We have carefully monitored the histograms $P(\rho)$ for different temperatures and chemical potentials. In all cases we have obtained only two peaks, and we have not found a triple-point behavior. However, it was impossible to state definitively whether or not a triple point exists here.

V. SUMMARY AND CONCLUSIONS

Using the hyperparallel tempering Monte Carlo and multiple-histogram reweighting techniques we have generated phase diagrams for different trimers adsorbed on a square lattice. We have assumed that a fluid molecule consists of two different segments *A* and *B*. We have considered three types of chains, namely, *BBB*, *ABB*, and *BAB*. We have analyzed behaviors of the linear and L-shaped rodlike molecules as well as perfectly flexible trimers. A three-centered potential with short-range attractive interactions, limited to nearest neighbors, has been used. The system is characterized by three energies of interactions between segments: u_{AA}, u_{BB}, and u_{AB}. In this study we have assumed that $u_{AA}=u_{BB}=-1$ and $u_{AB}=0$.

Notwithstanding the simplicity of the model we have formulated some significant conclusions about the influence of the internal structure and geometrical shapes of molecules on phase behavior of the two-dimensional films. The present study clearly shows that the shape of homogeneous molecules *BBB* affects the phase diagrams and critical parameters. The chemical structure of particles also plays a crucial role in phase transitions of one-component fluids consisting of short chains. In the case of heterogeneous trimers the shape of rodlike molecules is even more important for phase equilibrium. The shape of molecules can dictate the phase diagram topology. For certain heterogeneous isomers we have observed the existence of various ordered structures in the dense phase even at high temperatures. In this case phase diagrams of a special class have been obtained. These phase diagrams were asymmetrical, the critical density is shifted to unity, and the critical temperature is high. For the L-shaped *ABB* trimers there is no such privileged structure in the system and the phase diagram was similar to that obtained for homonuclear molecules. A very interesting phase diagram has been estimated for linear molecules *BAB*. We have found a second-order structural transition between disordered and ordered fluids above the vapor-liquid critical temperature. We suppose that *BAB* linear trimers exhibit the tricritical-point behavior.

In summary, the investigation shows that geometrical shapes and chemical structure of molecules are significant parameters determining phase equilibrium in a single-component fluid. Our results provide the picture of a much more complicated phase behavior of one-component two-dimensional films than was previously believed.[49]

ACKNOWLEDGEMENTS

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