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Phase behavior of associating liquid mixtures

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We present computer simulation results for the phase behavior of a liquid mixture with nonspecific dispersive interactions and directionally specific hydrogen bonds. The mixture exhibits complex closed loop phase behavior, which is in good qualitative accord with past theories. In addition, the model predicts the formation of self-assembled supramolecular structures at low temperatures in agreement with experiment.
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Liquid mixtures generally are homogeneous at high temperatures and only demix when cooled below an upper critical solution temperature (UCST) [1]. This behavior reflects a dominance of entropy at high temperature, which prefers mixing, but the control of unfavorable unlike pair interactions at low temperature, which cause demixing. In contrast, the behavior of liquid mixtures that phase separate on heating, i.e., ones showing lower critical solution temperatures (LCST), cannot be explained in this framework [1,2]. Some other factor, e.g., hydrogen bonds [3–9], or differences in shape, size, or compressibilities of the constituents [2,10,11], has to be evoked to explain this more complicated behavior.

The phase coexistence of pure materials [12–14] and mixtures [3–9] with site-specific hydrogen bonds (HB) have been of continuing interest. Mean-field models [4–7] incorporating the essential ingredient of a HB system, i.e., that a molecule can participate *at most* in a certain number of HB interactions, have been constructed. This ''saturation'' feature crucially accounts for the collective nature of HB systems, as can be illustrated in the case of molecules which can form exactly one HB. The formation of a HB between two molecules immediately precludes the formation of any other HB by the molecules of interest. In other words, the interaction between molecules is not pairwise. While these models have predicted rich behavior, including LCST and closed loop phase diagrams, it is unclear if these are artifacts of their mean-field character. A second approach, which avoids the mean-field approximation [8], involves mapping the HB system into the Ising model by using a decorated lattice formulation. An auxiliary sublattice, representing the hydrogen bonds, is introduced. Summation over this sublattice yields the effective coupling between the spins of the main lattice, J, which is a function of the temperature. Since the behavior of an Ising system is known, we have ''exact'' information about this model. However, the cooperativity inherent in HB systems is lost when the sublattices are summed out. The point to be stressed is that, while there has been considerable interest in HB systems, their theoretical understanding is incomplete at this time.

Here we present results derived from Monte Carlo (MC) simulations for the phase behavior of lattice mixtures which incorporate hydrogen bonding and nonspecific dispersive interactions. We find that closed loop phase behavior is a ubiquitous feature of these models, in qualitative agreement with mean-field theories [4–7]. In addition, we find a previously unanticipated formation of self-assembled ordered phases at low temperatures. These results rationalize recent experiments that demonstrate that molecules with multiple hydrogen bonding sites spontaneously self-assemble into myriad supramolecular structures [15–18].

As in our past work on surface behavior we consider a completely filled cubic lattice with its sites occupied by either A or B molecules [19]. We model *symmetric* mixtures where the interactions between any pair of A molecules and any two B molecules are identical. The molecules interact through isotropic nearest neighbor interactions characterized by the energy scale: $\chi \equiv (d/2k_BT)(2\epsilon_{AB}-\epsilon_{AA}-\epsilon_{BB})$. d is the coordination number (=6), and ϵ_{ij} is the interaction energy between a nearest neighbor $i-j$ pair. Therefore, $\chi \equiv 6/T^\star$ where $T^\star = k_BT/(\epsilon_{AB}-\epsilon_{AA})$. In this work we consider the case where $\chi > 0$, i.e., the dispersive interactions between unlike molecules are *unfavorable*. Each molecule has one ''donor'' and one ''acceptor'' that can participate in nearest neighbor HB. Since the molecules are structureless, the donors and acceptors do not have prespecified locations. The HB interactions are described by two equilibrium constants $k_{AA}(\equiv k_{BB})$ for the bonds between an A (B) donor and an A (B) acceptor on different molecules, and k_{AB} for bonds between A and B particles (either one being the donor). $k_{ij} \equiv P_{ij} e^{-E_{ij}/k_BT}$. The Helmholtz energy change in the formation of an ij HB is $\Delta A_{ij}(\mathrm{HB}) \equiv -k_BT \ln k_{ij}$. We have introduced the prefactor, P_{ij}, in the definition of k_{ij} to account for the loss of entropy associated with the formation of HB. This factor is not accounted for *a priori* in our model since the HB sites can assume arbitrary positions on the unstructured molecules without any penalty.

The simulations employ periodic boundary conditions in all three directions. Phase coexistence is located through the semigrand ensemble method [20] by scanning the exchange chemical potential, $\Delta\mu \equiv \mu_A - \mu_B$, in a series of simulations. μ_i is the chemical potential of species i. The composition of the mixture, $x_A = N_A/(N_A+N_B)$, where N_i is the number of i particles, is variable and the binodal is determined from histograms of its distribution, $P(x_A)$. $P(x_A)$ has a single maximum in the single phase. In the immiscible regime two maxima, each corresponding to one of the coexisting phases, are observed. An elementary MC move is to change the iden-

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TABLE I. Potential parameters and critical transition temperatures.

Set	K_{AA}	K_{AB}	UCST	LCST	T_{eq}
1	0.0134exp(1.8/T)	0.0134exp(2.0/T)	2.20 ± 0.10	No	No
2	0.0275exp(1.8/T)	0.0134exp(3.824/T)	2.20 ± 0.10	No	0.64 ± 0.02
3	0.0275exp(1.8/T)	0.0134exp(4.5/T)	1.94 ± 0.04	1.02 ± 0.02	0.78 ± 0.02
4	0.0134exp(1.8/T)	0.0134exp(5.0/T)	No	No	0.80 ± 0.02

tity of a randomly chosen particle. Another elementary move consists of the creation or elimination of a HB. The moves are accepted following the Metropolis criterion [20]. In the case where only dispersive interactions are changed by an elementary move, the probability of its acceptance is $\propto\exp(-\beta\Delta U)$, where ΔU is the energy change and $\beta=1/k_BT$. In contrast, when a HB interaction is created without any change in dispersive interactions then the acceptance probablity is $\propto\exp[-\beta\Delta A_{ij}(\text{HB})]\equiv k_{ij}$. Far from the critical points the MC runs consisted of 2.56×10^6 identity exchanges, and an equal number of HB creation/destruction moves per site. Near the critical points the runs were ten times longer. The critical temperatures, which are defined as the maxima of susceptibility [21], are shown in Table I. We have considered system sizes of $8\times8\times8$ and $16\times16\times16$, and the difference in critical temperatures between the two sizes are smaller than the reported uncertainty. A systematic study of the finite-size effect is planned for future work. A system with no HB interactions would correspond exactly to a three-dimensional Ising model with a critical temperature of $T_0^\star\approx2.25$. This simpler system would be *partially miscible* at all lower temperatures.

In Figs. 1 the binodals for all cases in Table I are shown. We shall focus on Fig. 1(c), which displays the richest phase behavior, i.e., a closed loop phase behavior.

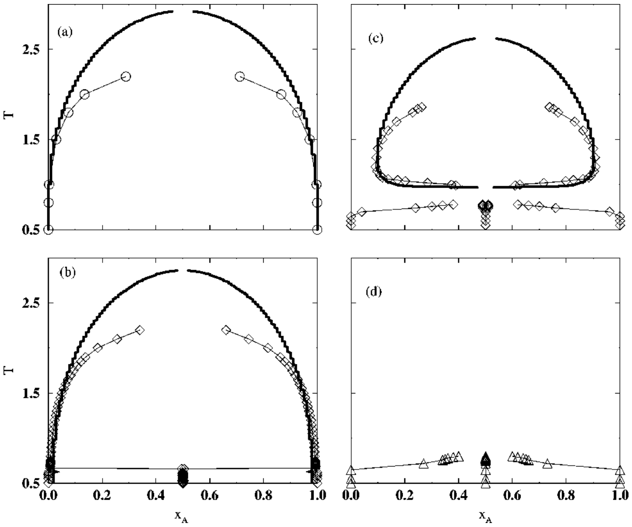

FIG. 1. Binodal curves for the four different sets of parameters listed in Table I. The points are Monte Carlo results and the thin lines are guides to the eye. The error bars are smaller than the points. The heavy lines are predictions of the theory of Veytsman [6]. The four different plots correspond to the four different sets shown in Table I: a corresponds to Set 1, b to Set 2, c to Set 3, and d to Set 4.

At high temperatures entropy dominates and the system is homogeneous. As the temperature is decreased, unfavorable dispersive interactions become important and the system phase separates with a well defined UCST. As the temperature is decreased further, HB interactions, which increase exponentially with $1/T^\star$, become more relevant. Since *AB* HB are strongly preferred over *AA* and *BB* HBs in Set 3 of Table I, they can overcome the unfavorable dispersive interactions and cause the system to remix at temperatures below the LCST.

With further reductions in temperature the conflict between the HB's, which prefer *AB* contacts, and the dispersive interactions, which would cause phase separation, become more important. The ground state of this system (i.e., $T^\star=0$), which would be obtained by minimization of the total *energy*, corresponds to a bilayered structure as shown in Fig. 2. In this ordered structure each site has all neighbors, except one, of its own kind. The dispersive interaction with this one unfavorable contact is compensated by the formation of the two favorable AB HB's. This layered phase is in equilibrium with a disordered phase rich in either one of the two pure components for all temperatures lower than T_{eq}, the *equal concentrations point* as defined by Landau and Lifshitz [22]. At T_{eq} the compositions of the coexisting phases are equal, but they are distinguishable because of their different symmetries. Note that the binodals of this first order transition are symmetric about $x_A=1/2$, and occur at $\Delta\mu\equiv\pm|\Delta\mu_c|$

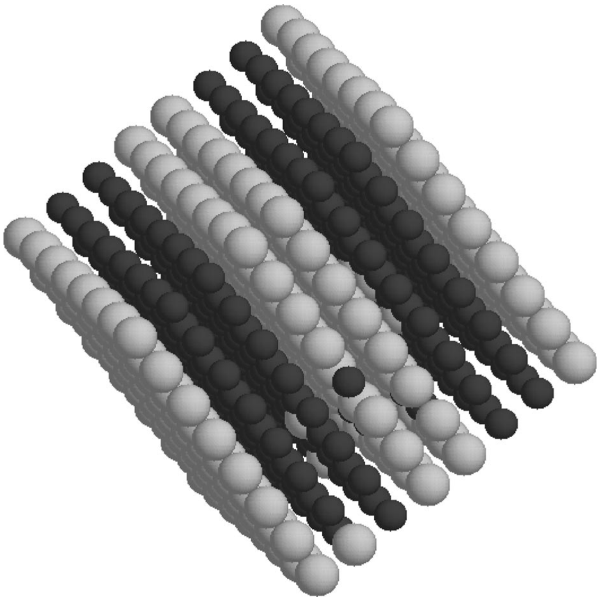

FIG. 2. Snapshot of ordered phase for Set 3 in Table I at $T^\star=0.55$.

$\neq 0$, corresponding to coexistence with a *A*-rich or a *B*-rich phase. To provide a zeroth order estimate of T_{eq} we consider the following facts. At T_{eq} a system with $x_A = 1/2$ can either exist as a disordered structure, or as the layered phase in Fig. 2. For simplicity, we assume that all HB are only of the *AB* type and are identical in number in both phases. Since each *A* molecule has, on average, three *B* contacts in the disordered state but only one *B* contact in the ordered phase, each molecule gains a nonspecific energy of $(\epsilon_{AB} - \epsilon_{AA})$ on ordering. However, it loses $k_B \ln 2$ in translational entropy and $k_B \ln 3$ in rotational freedom in picking unlike HB sites when it orders. Therefore, $k_B T_{eq} \ln(6) = \epsilon_{AB} - \epsilon_{AA}$, which yields that $T^{\star}_{eq} \approx 0.55$. While this procedure underestimates the real equal concentrations temperature (see Table I), several approximations have been made. These include the assumption that the number of *AB* HB do not change on ordering, as well as the fact that all unlike neighbors of a molecule, assumed to be three in the disordered phase, are open for HB interactions with the molecule of interest. However, this estimate for T_{eq} is a reasonable descriptor for the physics of this situation.

We now consider the other sets in Table I. As the HB between dissimilar monomers are made less favorable than in Set 3, the LCST disappears. This is because the *AB* HB are not strong enough to overcome the unfavorable dispersive interactions and miscibilize the mixture. In set 2 the system merely displays UCST behavior which merges with a equal concentrations point at low temperatures. Further reductions in the *AB* HB strength prevents the system from displaying an ordering transition as well (set 1). In this situation the unfavorable dispersive interactions dominate, and the system behaves very similar to a mixture with no HB. Evidence of the unimportance of the HB is the fact that the UCST in Set 1 is approximately equal to that obtained from the three-dimensional Ising model. In the opposite case when *AB* HB are made even stronger than in Set 3, the closed loop becomes smaller and can even disappear as shown in set 4. In this situation the HB between *AB* pairs is too strong relative to the dispersive interactions at all high temperatures. However, we have an ordering transition at low temperatures, which reflects the competition between *AB* HB and the unfavorable *AB* dispersive interactions. Notice that all of the situations where *AB* HB are stronger than Set 1 have an ordering transition, since the ground state always prefers the formation of these ordered phases in this region of parameter space.

The MC generated phase diagrams are in qualitative agreement with the mean-field model of Veytsman [6] which explicitly accounts for the saturation feature of HB systems (see Fig. 1). Note that the mean-field model, which assumes that all phases are isotropic, cannot capture the presence of ordered phases. Consequently, this model does not offer any explicit prediction for T_{eq}, as well as any equilibrium between order and disordered phases. Apart from this drawback, the mean-field approximation only serves to cause *quantitative* inaccuracies in predicting the phase diagrams in these situations.

Next we note that incompressible mixtures on a lattice are isomorphic with compressible pure components. This mapping is particularly relevant since recent calculations have shown that compressible lattice models, with dispersive interactions and site specific bonds, could capture the liquid-liquid phase equilibria observed for pure water and silicon [13]. Two points need to be stressed here. The model used by us is simpler than those utilized previously for these pure materials, since it does not involve two hydrogen bonded sublattices [12]. Consequently, our simpler model demonstrates the generality of the existence of liquid-liquid coexistence for pure materials. Second, our calculations show that transitions between ordered and disordered states occur at lower temperatures. Such ideas could be relevant to understanding the crystallization of associated liquids at low temperatures. To our knowledge, such calculations have not been conducted to date.

A final point is the connection of the self-assembly in HB systems to those observed in block copolymers [23], surfactants [24,25] and in charge frustrated systems [26]. In the block copolymer and surfactant sets the constraint that overcomes the ‘‘dislike’’ between the head and the tail moieties, and ensures the formation of mesophases, is the covalent connectivity between the two groups [24,25]. Similarly, in charge frustrated systems the constraint of electroneutrality ensures that these systems assemble spontaneously into mesophases [26]. In the sets considered here, the HB may be thought of as bonds between dissimilar molecules whose strength becomes stronger with decreasing temperature. Consequently, the self-assembly in all of these cases is a compromise between two competing interactions.

In summary, we have presented the phase behavior of associating fluid mixtures. Experimentally observed closed loop phase diagrams and formation of self-assembled phases are reproduced by this simple model. Since past theories are able to qualitatively reproduce the location of the critical points of the closed loop phase diagrams we conclude that the mean-field approximation evoked by these models do not introduce artifacts. A previously unanticipated formation of self-assembled supermolecular structures is in good agreement with experimental findings [5]. Of course, the particular layered symmetry of the self-assembled phases is imposed by the cubic lattice and the fact that particles are ‘‘structureless.’’ This prompts further study of the effect of molecular structure on the symmetry of the self-assembled phase, an issue we shall focus on in future work.

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