Liquid-Liquid Immiscibility in Pure Fluids: Polyamorphism in Simulations of a Network-Forming Fluid

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We report Monte Carlo simulations that show both vapor-liquid and closed-loop liquid-liquid equilibrium in a pure substance, for a model fluid that forms orientation-dependent intermolecular bonds. This is the first time that direct evidence of liquid-liquid immiscibility in a pure fluid has been found using exact methods. Because the model is formulated in terms of a tetrahedrally coordinated molecule, the results are relevant to a broad class of substances, particularly to the transitions between amorphous phases which are known to occur in H_2O, SiO_2, and GeO_2. [S0031-9007(96)01741-3]

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Transitions between distinct amorphous forms of pure substances are not uncommon [1]. In the liquid phase, examples include semi-conductor/metal transitions, e.g., Te [2], Se [3], and Bi [4]; and metal-insulator transitions, e.g., Cs [4] and S [5]. Transitions also occur between amorphous solid phases, e.g., Ge and Si [6]. Generally such transitions are higher than first order, and structural changes are not accompanied by volume and enthalpy discontinuities [7]. In network-forming fluids [8], polyamorphism generally involves amorphous solids, e.g., SiO_2 [9] and GeO_2 [10,11].

The existence of different amorphous states, though unusual, is not extraordinary. However, the apparently first-order transition between low-temperature amorphous states in H_2O [12,13], which differ in density by more than 25%, has led to the hypothesis that polyamorphism in water has its basis in an underlying equilibrium phase separation [6,13,14]. This implies the possibility of a first-order liquid-liquid transition in a pure substance. Support for this viewpoint comes from experiments in which a sharp transition occurs between a low density and a high density form of amorphous solid water (LDA and HDA, respectively). The LDA/HDA transition is marked by discontinuous changes in specific volume and enthalpy which are reproducible and reversible except for hysteresis due to long relaxation times for these glassy phases [12,13]. This transition has also been monitored spectroscopically as a function of time by Balagurov *et al.* [15]. Thus experimental evidence is not inconsistent with the existence of a first-order transition between two distinct, disordered forms of metastable water, of which the observable LDA/HDA transition is the arrested manifestation. From a theoretical perspective, a first-order transition between distinct forms of liquid water is an essential feature of one of the thermodynamically consistent scenarios that have been invoked to explain the anomalous properties of supercooled water [16,17].

The transitions between polyamorphic phases in other network-forming substances [9,10] are less abrupt than in water. There are, however, striking similarities between the transitions occurring in H_2O, GeO_2, and SiO_2; in each case there is a competition between open networks with low coordination numbers and collapsed structures having high coordination numbers [9,11,18,19]. It is then reasonable to expect that if a liquid-liquid separation is the underlying cause of polyamorphism in water, this phenomenon could be of more general relevance to understanding the global phase behavior of network-forming fluids.

A number of computational [16,17,20] and theoretical [21–25] studies have addressed the possibility of liquid-liquid immiscibility in pure substances. Molecular dynamics simulations of deeply supercooled water [16,17,20] have provided indirect evidence of a phase transition, but the glassy nature of the states involved has prevented an unambiguous calculation of the equilibrium properties of the coexisting phases. Some theoretical models, both for generalized [21,22] network-forming fluids and specifically for water [23,24], do predict a phase transition between two liquids at low temperatures. Solutions to these models, however, have all used approximate methods. They can be classified in one of the following categories: The model was based upon a detailed microscopic Hamiltonian, and the partition function was estimated using approximate techniques [21]; a bulk-density-dependent approximation was used to describe orientational bonding, in conjunction with a mean-field equation of state [22,23]; or a pure fluid was treated *a priori* as a mixture of molecules which can be in one of two "states," where the states are related to bulk thermodynamic properties [24]. It should also be noted that there are theoretical models that predict liquid-liquid equilibrium in a pure substance for fluids which are not network-forming [26,27]; however, these, too, have been solved approximately. The work reported here shows that pure-fluid liquid-liquid equilibrium (LLE) occurs in a general model of network-forming fluids when solved without the use of approximate techniques [i.e., via Monte Carlo (MC) simulation].

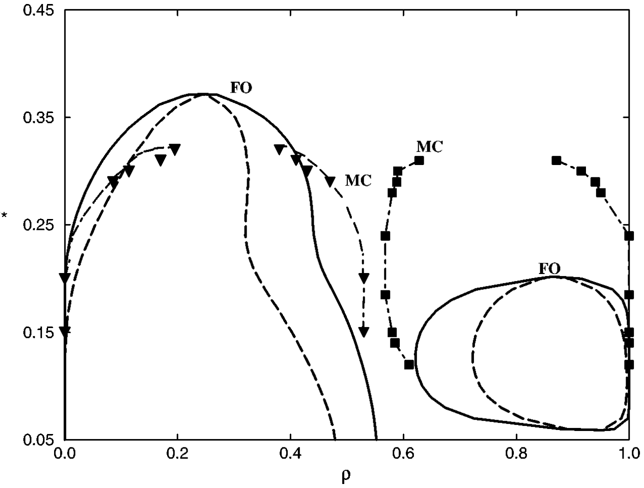

FIG. 1. Fluid-phase boundaries for $\epsilon/J = 0.2$, $c = 0.8$, $q = 108$ from MC simulation (filled symbols) and from the FO solution (solid lines); dotted lines indicate the stability limits predicted in the FO solution. Dot-dashed lines are guides to the eye.

The model is described in detail in Ref. [21]. To summarize, molecules interact via nearest-neighbor (*nn*) attractions and strong, orientation-dependent intermolecular bonds which are weakened when other molecules occupy the sites which are closest to a formed bond (on the BCC lattice, there are six sites other than the bonding pair that encircle any possible bond; each of these sites, when occupied, weakens that bond). The molecules lie on sites of a BCC lattice, with each site being either vacant or occupied by a single molecule. Each molecule has q possible, distinguishable orientations, of which only a small number are correct for bonding with a *nn* molecule. The parameters of the model are the number of distinguishable orientations for a molecule q, the nn attraction energy $-\epsilon$ (which is independent of orientation), the bond energy $-J$, and the fraction c $(0 < c < 1)$ of the energy of a bond which is lost when the maximum possible number of molecules are packed into the above-defined region surrounding that bond (each of the weakening sites when occupied, increases the bond energy by $cJ/6$) [21]. Molecules are able to rotate about their sites and are not constrained to point their arms toward the *nn* sites, except when involved in one or more bonds. A bond forms only when a donor arm of one molecule is aligned with an acceptor arm of a neighboring molecule. The ground state of the model is an ordered, space-filling tetrahedral network with a density (i.e., fraction of sites occupied) of $\frac{1}{2}$, and with all molecules having four, full-strength bonds; this favors bonded networks in disordered phases at low temperatures.

In [21], zeroth-order (ZO) and first-order (FO) solutions were reported for this model. In the FO approximation, LLE was found to arise from a competition between a low-density fluid with a high degree of bonding (i.e., low energy and entropy) and a high-density liquid with little or no bonding (i.e., high energy and entropy). Note that the model is formulated only in terms of microscopic interactions, i.e., without using bulk-density-dependent interactions [22,23], and without assuming specific states for the molecules [24]. A representative phase diagram in the temperature-density ($T\rho$) plane is shown in Fig. 1. Note the miscibility gap at low temperatures and high densities. The FO approximation does not account for long-range order, and so does not indicate if the liquids are metastable with respect to solid phases [21]. It is important to note that the LLE has both upper and lower critical temperatures (UCT and LCT). This is a consequence of the essential role of entropic contributions to the free energy of the high-density liquid [21]; in contrast, if LLE is stabilized only energetically, immiscibility persists at low T [23,28].

The MC simulations described here were performed in the canonical ensemble (fixed particle number N, number of sites B, and T) for a lattice consisting of 512 ($8 \times 8 \times 8$) BCC unit cells, using a Metropolis algorithm and periodic boundary conditions [29]. Phase coexistence and the values of ρ ($\equiv N/B$) for coexisting phases at a given T were determined from block-density distribution functions [30–32]. In this method a block or subcell of b sites ($b \ll B$) was chosen randomly in the simulation box for a given configuration after first equilibrating the system. This was repeated between five and ten times for each configuration, for a series of equilibrated configurations. Recording the number of occurrences of each value of the subcell density (ρ_i) yields the block-density distribution $P_b(\rho_i)$. When the choice of (N,B,T) is a state point within the unstable portion of a two-phase region, $P_b(\rho_i)$ is bimodal, with the values of ρ_i at the peaks corresponding to the values of ρ for the two coexisting phases [30,33] (e.g., ρ_v and ρ_L for VLE, or ρ_{L1} and ρ_{L2} for LLE).

Typical MC runs consisted of 10^6–10^7 MC steps for equilibration (with as many as 5×10^7 steps needed at the lowest values of T). $P_b(\rho_i)$ were collected by recording ρ_i in five to ten randomly chosen subcells, within each of 0.5–1.0×10^6 configurations generated after equilibration. Preliminary runs showed that $24 \leq b \leq 40$ provided reasonable ρ_i resolution without encountering problems with phase separation within the subcell. All results reported here are for $b = 35$.

$P_b(\rho_i)$ were collected for a series of T and ρ, such as those shown in Fig. 2. The densities of the coexisting phases determined from $P_b(\rho_i)$ for both VLE and LLE are shown in Fig. 1 with the FO prediction for comparison. The statistical uncertainty of the density values were calculated to be less than 2% from repeated runs at the same conditions. As noted in [30], the block-distribution method becomes increasingly ambiguous near critical points. This made determination of densities of the two phases unreliable for $|T^* - T_c^*|$ less than 0.01 ($T^* \equiv$

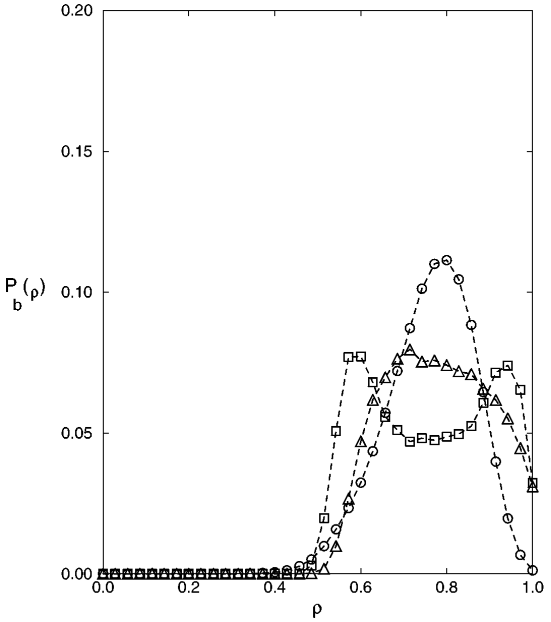

FIG. 2. Block-density distributions for $b = 35$, $\rho = 0.76$, with $T^* = 0.32$ (circles), 0.29 (squares), and 0.10 (triangles). Note that both high and low T^* distributions are unimodal, indicating that both upper and lower critical points exist for the LLE. Model parameters are the same as in Fig. 1.

kT/J). Using the T^* values at which $P_b(\rho_i)$ first becomes unimodal as T^* is raised or lowered from within the two-phase region (see Fig. 2), we were able to bracket the values of the critical temperatures within the following ranges: $0.31 < \text{UCT} < 0.32$, $0.10 < \text{LCT} < 0.11$, and $0.32 < T_c^*$ (vapor-liquid) < 0.33 for the case shown in Fig. 1.

In Fig. 1 the important MC results are the existence of multiple phase transitions between disordered phases in a pure fluid, the closed-loop form of the LLE, and the qualitative agreement with the FO approximation. The existence of the LCT is indicative of the strong role of the orientational entropy which stabilizes the high-density, unbonded liquid (L2) relative to the low-density, highly bonded (low-energy) liquid (L1).

It was noted in preliminary simulation runs that at the lowest temperatures phase separation occurred between a low density crystal and a high density liquid. This was apparent in that a large fraction of the simulation box consisted of connected regions having the structure of the low-density ground-state, while the remaining regions were relatively disordered, with an average ρ greater than the value of N/B in the simulation. Thus the crystalline phase is the state of minimum free energy in this region, and LLE under these conditions of T^* and ρ necessarily occurs between metastable phases. In order to study the thermodynamics of metastable phases, it is necessary to constrain the system so as to prevent nucleation of the stable phase [34]. In the present work, this was done by rejecting configurations in which at least one cluster of molecules exceeded a maximum crystalline-cluster size N_c^m. In the crystal which forms here, each molecule has four full-strength bonds, and thus is bonded to four *nn* molecules and has no bond-weakener sites occupied. The size of a crystalline configuration is defined by the number of molecules it contains that are simultaneously bonded to each other and have four full-strength bonds. In principle there is a critical value of N_c^m, the critical nucleus size $N_c^{m,*}$, above which crystallization is spontaneous. The dependence of $N_c^{m,*}$ on T^* and ρ below the equilibrium melting line $T_m(\rho)$ is not known *a priori*. Rather than attempt to determine $N_c^{m,*}$ as a function of T^* and ρ [35], we performed simulations over the full range of T^* reported in Fig. 1 with $N_c^m = 1$; and tested the effect of varying N_c^m at selected T^*. At $T^* \approx$ UCT the values of ρ_{L1} and ρ_{L2} are independent of N_c^m. For $N_c^m = 1$, 2 the LCT was unchanged (within the 0.01 T^* bracket noted above). The LCT apparently shifts to lower T^* as N_c^m is increased above 2. The LLE bimodal curves with $N_c^m > 2$ were qualitatively the same as those for $N_c^m \leq 2$ (maximum N_c^m used at $T^* = 0.1$ was 4), in that $\rho_{L2} - \rho_{L1}$ decreases with decreasing T^* for T^* less than $\lesssim 0.15$. However, we were unable to determine more precisely the value of the LCT when $N_c^m > 2$ because of prohibitively long simulation times needed to sample ergodically at the low T^* where the LCT is apparently located [36]. We conclude that the closed loop form of the LLE is not an artifact of using too severe a constraint, but that determination of $N_c^{m,*}$ as a function of T^* and ρ in the vicinity of the lower critical point will be necessary to find the exact value of LCT.

In summary, we have presented results of MC simulations which show closed-loop, pure fluid LLE for a model network-forming fluid that is deeply supercooled. This represents the first direct evidence of a true first-order transition between disordered phases in a model system of a pure substance, obtained without using approximate solution techniques. Additionally, the simulation results support the mechanism proposed recently [21] to account for the existence of both UCT and LCT in this phase transition. The transition occurs because of the gain in entropy that results from the disruption of the network structure in going from L1 to L2. The general nature of this model suggests that such complex phase behavior may be relevant to a broad class of fluids in which the local density and the degree of intermolecular bonding are strongly correlated. This supports the argument that polyamorphism in glasses may have its basis in an arrested LLE.

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[1] In what follows we use the term polyamorphism to indicate the existence of a transition between distinct disordered phases of a pure substance, in addition to the vapor-liquid transition.

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