Multiple Ordering Transitions in a Liquid Stabilized by Low Symmetry Structures

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We present a numerical study of a lattice model of a liquid characterized by a low-symmetry favored local structure. We find that the freezing point is depressed far enough to reveal an exotic liquid-liquid transition characterized by the appearance of an extended chirality, prior to freezing. The ordered liquid can be readily supercooled to zero temperature, as the combination of critical slowing down and competing crystal polymorphs results in a dramatically slow crystallization process. These results provide an explicit scenario by which the ordering of a liquid can proceed via an intermediate liquid-liquid transition, a scenario that may prove helpful in the analysis of low temperature liquids interacting by more realistic interactions.

A tray of coins of the same size will, when gently shaken and inclined, organize into a regular triangular lattice. This spontaneous appearance of an extended structure can be rationalized in terms of the high symmetry of the particles involved and the spatial homogeneity that such symmetry implies. Replace the coins in the tray with jigsaw puzzle pieces, even identical ones, and any expectation of periodic ordering is greatly diminished. Why? The absence of a sufficiently well packed crystal structure, the competition between different local arrangements, the slow kinetics of rearrangement and the increased entropy of the disordered state are all plausible reasons for the failure of ordering of the puzzle pieces. The very number of possible explanations highlights our uncertainty about collective ordering when low symmetry particles are involved. Extensive theoretical studies of a variety of liquid crystal phases—nematic [1], cholesteric [2], discotic [3], and cubic [4]—have provided deep insight into the order associated with anisotropic particles that retain a degree of rotational and reflection symmetry (or, in the case of cholesterics, a perturbation from such symmetries). The kinetic stability of molecular glass-forming liquids has long been loosely attributed to some combination of low symmetry and conformational flexibility.

We are interested in the behavior of a liquid for which all geometric symmetries are absent at the local level. The absence of reflection symmetry implies that the favored local structures are chiral. We consider a simple lattice model with a restricted set of configurations, each site being occupied by one of two objects (which we shall call spin-up or spin-down). For a given lattice we can enumerate every distinct configuration of the nearest neighbors to a given site. We select the favored local structure by picking

one such neighborhood configuration and assigning it an energy of -1, while all other local arrangements are given an energy zero [5]. We consider here the case of a 2D triangular lattice and its only possible pair of chiral local structures, with a single enantiomer favored (see Fig. 1). A discussion of the behavior of the 3D face-centered cubic lattice and its 39 pairs of chiral local structures will appear elsewhere. We have previously studied the ground states [5], liquid entropy [6], and the freezing transitions [7] in the 2D lattice model for the nonchiral local structures and have shown that freezing occurs with little or no evidence of supercooling for all nonchiral favored local structures. In this Letter we report on the dramatically different situation observed in the case of the least symmetric favored local structure.

In Figure 2 we plot the average energy E at equilibrium (thick blue line) and the heat capacity $C_V = \partial E / \partial T$ versus temperature for heating and cooling runs. We find clear evidence for two transitions in our model liquid. A second order transition occurs at $T_c \approx 0.325$ as indicated by the peak in C_V. It separates the high-temperature disordered
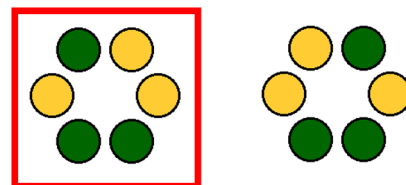

FIG. 1 (color online).   The pair of chiral local structures, with the favored enantiomer boxed (up-spins in yellow, down-spins in green). Sites whose local spin environment correspond to this favored local structure and its rotational variants (regardless of the site's own spin) are given an energy of -1.
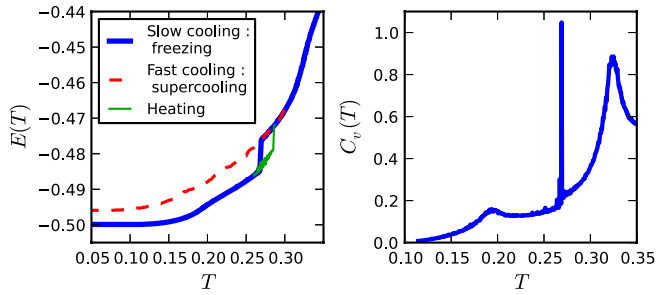
FIG. 2 (color online).   The temperature dependence of the average energy per site and heat capacity (second panel). The high-temperature regime, which is not displayed here, is characteristic of liquids showing strong accumulation of local structures prior to crystallization, as discussed in [6].

state from a more ordered liquid (whose order we describe below), as illustrated in Fig. 3(a). Below the second order transition, we observe, at sufficiently low cooling rates, a first order phase transition at $0.26 \leq T_f \leq 0.29$ associated with significant hysteresis. The first order transition corresponds to the liquid freezing into the polycrystalline ordered state depicted in Fig. 3(c). At faster cooling rates (dashed line in Fig. 2), the system gets stuck in a low-energy supercooled state, as depicted in Fig. 3(b). A third feature at $T \approx 0.19$ corresponds to a phenomenon within the crystalline phase. We believe that this heat capacity peak is associated with a qualitative change in the nature of grain boundaries that results in the removal of topological point defects at the transition, but have not sought to quantify this subtle effect.

The ground state energy of this system is $E_0 = -1/2$, which means that at most half of the lattice sites can

be simultaneously in the chiral favored local structure. This energy is considerably higher than that of the racemic mixture, for which $E_0 = -4/5$ [7]. The significant stability of the racemic crystal over that of the chiral structure is probably not a chance outcome. Over 90% of chiral organic molecules crystallize preferentially as racemic crystals consisting of equal numbers of both enantiomers [8]. We have identified, by construction, several crystal polymorphs with an energy $-1/2$, six of which are depicted in Fig. 4. We have, however, only ever observed the polycrystalline mixture shown in Fig. 3(c), which exhibits long-range anisotropy but no translational order. We distinguish the polycrystalline phase from the supercooled liquid by this anisotropy (by inspection) and the fact that the former has an energy of exactly $-1/2$ at $T = 0$ while the isotropic liquid energy is always greater. These states are separated by a well defined first order transition.

The freezing temperature T_f can be related to the change in energy ΔE and entropy ΔS on freezing by $T_f = \Delta E / \Delta S$. The central point here is that any geometric awkwardness that produces a high energy crystal will typically result in the depression of the freezing point. One consequence of the low freezing point is that, in extending the temperature range of the liquid, a greater accumulation of local structure will take place prior to crystallization. How much local structure a liquid can accumulate and how this accumulation ends are questions that have arisen in the study of supercooled liquids. Suggested end points for a supercooled liquid, as the fraction of favored local structure increases, are either an instability with respect to crystallization or the formation of a glass. In our model liquid we observe a third outcome,
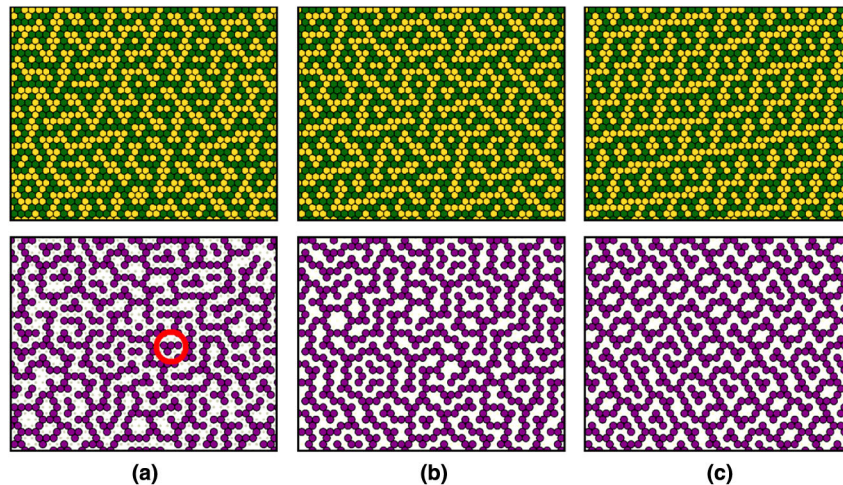

FIG. 3 (color online).   On the upper row are shown spin configurations of the system with up and down spins indicated by yellow and green . The lower row shows in purple the sites that lie in the FLS. (a) A liquid state just below the liquid-liquid transition. The liquid is highly structured, and has energy -0.47—that is, 47% of the lattice sites lie in the FLS. A chiral cluster of FLS, revealing the symmetry breaking, is circled in red. (b) A supercooled state at $T = 0$. (c) A crystalline state of energy $-1/2$. This state retains some freedom of configuration and extensive entropy, as it is a mixture of crystalline domains with no energy increase due to grain boundaries. However, it has long-range anisotropy, as opposed to the supercooled liquid.
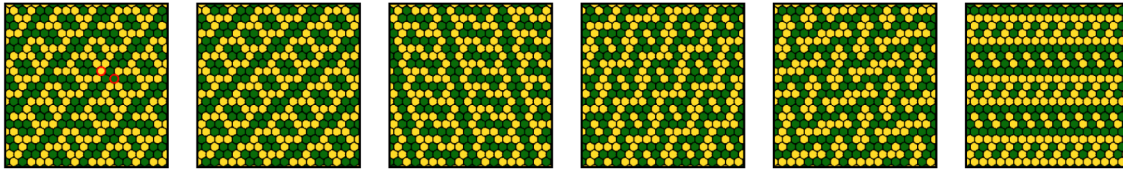
FIG. 4 (color online).   Some crystalline structures for the model, illustrating the structural complexity of the ground state. All these structures have an energy of $-1/2$ per site, and they are all anisotropic. Note that in the leftmost one, the two sites outlined in red can be flipped simultaneously at no energy cost. This implies an extensive entropy for the ground state of the system. Only the rightmost crystalline structure preserves the Σ symmetry.

a second order liquid-liquid transition that occurs at $T_c \approx 0.325$. Unlike the zero-field Ising model [9], our Hamiltonian is *not* symmetric with respect to spin inversion since the inversion of all spins will transform one enantiomer into the other, a transformation which will involve a change in energy as only one enantiomer is favored. The only elementary symmetry for our chiral Hamiltonian is the combination of a global spin inversion with a reflection through a line (we shall refer to this composite operation as Σ) as shown in Fig. 5. This symmetry is spontaneously broken at the second order phase transition. We identified the driving force for this symmetry breaking as the short-range entropic repulsion between favored local structures with different values for the central spin, using the formalism introduced in [6]. Applying the operation Σ we recover a configuration unchanged in energy but with a change in magnetization. It follows that magnetization (i.e., the difference between up and down spin concentrations) represents an order parameter for the second order phase transition observed in the chiral liquid. In Fig. 6 we plot the temperature dependence of the magnetization, which bifurcates as the temperature drops below T_c.

The two states of different magnetization below T_c correspond to the dominance of one of the two possible choices of handedness for the extended clusters of overlapping favored local structures, such as the cluster circled in red in Fig. 3(a). The onset of this structural chirality in the liquid can be measured by plotting the difference of density between this extended cluster and its enantiomer, which vanishes at high temperature due to the Σ symmetry, as shown in the right panel on Fig. 6. We categorize this transition as a liquid-liquid transition since translational disorder and isotropy are retained below T_c. We do not observe the global anisotropy characteristic of a liquid crystal,
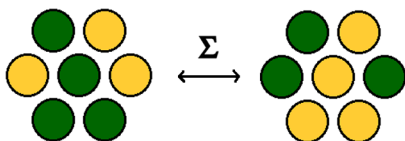
contrarily to cholesterics, for example, for which the chirality is accompanied by the anisotropy associated with the helical axis. It is well established [10] in crystals that the optical activity (an observable aspect of chirality) includes contributions from the global structure as well as from the purely local chirality. α quartz, for example, is chiral despite the fact that the elementary unit—the silica tetrahedron—is achiral. The low temperature liquid phase described here is, to our knowledge, the first example of a *liquid* whose chirality includes a contribution from the global structure.

The accumulation of local favored structures has, in supercooled liquids, been invoked as the origin of the substantial slowing down observed in these systems on cooling [12]. In the case of our model the temperature dependence of *some* relaxation times corresponds to the standard critical slowing down. The relaxation time τ_E obtained from the autocorrelation function of the energy fluctuations exhibits a divergence at the transition temperature, as shown in Fig. 7. At $T > T_c$, we find that the temperature dependence of τ_E when approaching the transition temperature T_c is well described by a power law $\tau_E \propto (T - T_c)^{-\gamma}$, where $\gamma \approx 1.9$, a value close to exponent 2 found for the critical slowing down in the Ising model on the 2D square lattice [9]. The decrease in τ_E as the temperature is lowered below T_c reflects the decreasing amplitude of the energy fluctuations. Not all time scales in the liquid are slaved to this critical slowing down. The persistence time, defined as the average lifetime of the individual spin states, shows no such singular temperature dependence (dashed line in Fig. 7). This is expected for a liquid-liquid transition: the spin structures are transient.

Another time scale of physical significance is that of crystallization. The first order phase transition at $T \approx 0.26$ is observed only for cooling rates slower than 10^8 Monte Carlo Metropolis steps per site and unit of temperature (for comparison, a cooling rate of only 10^4 leads to crystallization for more symmetric choices of the favored local structure in this model [5].) This tremendously slow process could be observed using a rejection-free Monte Carlo algorithm [11]. At a faster cooling rate, the system gets stuck in one of many supercooled metastable states. Note that the observed ground state, shown in Fig. 3, shares the same broken Σ symmetry as the liquid state

FIG. 5 (color online).   The only symmetry of the FLS, which we call Σ, consists of an inversion of all spins and a reflection.
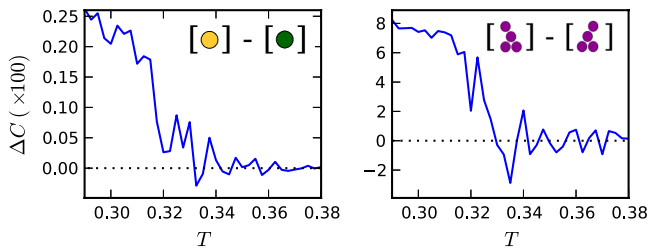
FIG. 6 (color online).   Left panel: The magnetization, defined as the difference of concentrations ΔC of up and down spins, as a function of temperature. Below the critical point T_c the magnetization deviates significantly from zero. Right panel: The extended chirality, defined as the difference of concentration of the two clusters of FLS as represented, exhibits the same behavior as the magnetization.

below T_c. This means that the crystallization rate will reflect the slow relaxation time of the structural fluctuations of the ordered liquid state. As shown in Fig. 2, there is substantial hysteresis in the $E(T)$ curves about the freezing transition. When a sufficiently slow heating rate is employed, melting is observed at a temperature well below T_c, establishing the separation of the two transitions.

The consequences of the low symmetry of the local stable structure can be summarized as follows. The crystal state has high energy, a large unit cell, and many polymorphs. Because of the high energy of the crystal, the stability of the liquid is extended to low temperatures so that it accumulates a considerable amount of locally favored structures. This high density of FLS ultimately drives the liquid-liquid transition reported here, associated with the appearance of an extended chirality of the liquid structure itself. The non-Arrhenius temperature dependence of relaxation dynamics of the liquid can be directly associated with the slowing down associated with this critical point. Crystallization from the ordered liquid is extremely slow, so that supercooled liquid states are readily observed, with an energy that closely approaches that of the crystal.

There is a considerable amount of literature on the buildup of local structures in liquids as they are supercooled and the possible consequences of this ordering [12], recently reviewed by Tanaka [13]. A number of liquids exhibit liquid-liquid transitions in either equilibrium (sulfur [14], phosphorous [15], and cerium [16]) or in the supercooled state (silica [17], water [18], silicon [19], and triphenyl phosphite [20]). In a number of cases the liquid-liquid transition appears to coincide with either the instability of the metastable state with respect to crystallization [21] or the glass transition [22]. In the case of a number of models of atomic mixtures, an accumulation of local order is observed without any sign of a liquid-liquid transition [12]. The low temperature fate of such liquids remains unclear—the possibilities include an instability with respect to crystallization (the Kauzmann solution), the arrest into a glass state or some order-disorder transition not yet observed. The model presented here provides
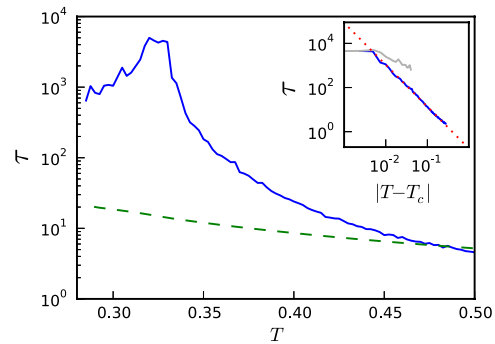

FIG. 7 (color online).   Solid line: the characteristic autocorrelation time of the energy of the system, measured in Monte Carlo Metropolis steps per site. It diverges at the second order phase transition, revealing critical slowing down. Dashed line: The spin persistence time, defined as the average time before a site flips. This quantity is not affected by the transition at T_c. Inset: The autocorrelation time in log-log scale. Dashed line: power-law fit $\tau = 0.17|T - T_c|^{-1.9}$ with $T_c = 0.325$. The agreement is excellent at $T > T_c$. The behavior at $T < T_c$ (light gray) remains unexplained.

a case study of a complex liquid in which these unknowns are explicitly resolved in the manner described in the preceding paragraph. The key feature of this liquid model is the separability of the liquid-liquid transition and crystallization, the two associated broken symmetries being sufficiently decoupled to permit the occurrence of the two distinct transitions. Which aspects of a Hamiltonian determine whether this decoupling occurs or not is, we suggest, an important question for future research into the low temperature fate of supercooled liquids.

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