The variety of ordering transitions in liquids characterized by a locally favoured structure

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The Variety of Ordering Transitions in Liquids Characterized by a Locally Favoured Structure

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We present a new lattice model of liquids in which the energy of a configuration is determined by the local coordination environments rather than pairwise interactions. This model is used to explore how the accumulation of order on cooling depends on the geometry of the locally favoured structure. We find that, while high symmetry local structures result in ordering that occurs predominantly via a thermodynamic freezing transition, liquids characterised by a low symmetry local structure exhibit a significant increase in local order on cooling before crystallizing.

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Structural studies of deeply supercooled liquids have confirmed the existence of favoured local structures. These structures exert a dominant influence in the kinetic properties of the liquid [1, 2], provide a valuable resolution of liquid structure [3] and have been invoked in accounting for a liquid's glass forming ability [1, 4, 5]. If the potential energy landscape of a liquid has minima characterised by a particular favoured local structure, then we are confronted by a number of interesting and fundamental questions. What is the relationship between the favoured local structure of the liquid and the structure of the crystal into which it freezes? How does the existence of local structure in the liquid influence the nature of the freezing transition? How, if at all, does the specific nature of the favoured local structure influence the properties of the equilibrium liquid? To address these questions, we introduce a new lattice model of a liquid in which a favoured local structure (FLS) is explicitly specified so that a range of distinct geometries of the FLS can be explored.

If one considers the physical implication of the view of that liquids can be characterised by favoured local structures then we would have to conclude that a preferred local structure can be selected without having to invoke the statistical benefits associated with global order. This means that the FLS should be more properly regarded as a property of the short range interactions of the Hamiltonian rather than of the N-body partition function. We shall adopt this perspective to study the consequences of a favoured local structure.

From the perspective of locally favoured structures, the existence of metastable liquids at temperatures below the freezing point poses the following question. If the FLS stability does not depend on cooperativity, what prevents them simply aggregating continuously for any supercooling? Frank's elegant 1952 contribution [6] to this question (at least for a liquid of a single spherical species) was to point out that a FLS in the form a regular icosahedral coordination shell would be both low energy and, due to the 5-fold symmetry, unable to periodically tile space (an example of geometric frustration [7, 8]). This suggestion has inspired a considerable body of work in which the observation of icosahedral FLS's in a supercooled liquid is associated, to varying degrees, with the stability of the supercooled liquid [2, 4, 5, 9].

To carry out a systematic study of the role of the local geometry on the stability of the liquid and the nature of the freezing transition, we shall introduce a lattice model of a liquid in which the energy of the spin configuration is determined by the local coordination geometries instead of pairwise interactions between spins. This model makes use of the proposition, previously mentioned, that the favoured local structure could be completely determined by the Hamiltonian. We neglect any modification of this favoured structure due to cooperative effects of the surrounding material. Consider a set of Ising spins on a 2D triangular lattice. The local environment of a site is defined as the set of spin states of its six nearest neighbours. Out of the 2^6 possible neighbour spin configurations, we can identify 13 distinct structures where 'distinct' means structures that are not related by a rotation. Of these 13, there are 5 pairs of local structures that are spin inversions of each other. Since we attach exchangeable roles to both spin values, we only need study one of each of these related pairs. This leaves us with a selection of 8 favoured local structure (FLS) and these are sketched in Figure 1 with the labeling scheme is explained in the caption. Each site of the system will be assigned an energy -1 if its environment is in the FLS and an energy 0 otherwise, irrespective of the sign of the spin on that site. One local structure, labeled $\{32\}$, has no plane of symmetry and is therefore chiral. In this paper we have chosen to neglect this difference and, when the $\{32\}$ structure is chosen as the FLS, we have assigned an energy of -1 to both enantiomers.

The groundstates are the maximum density packings of

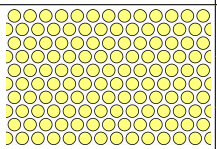
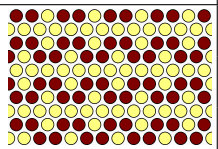
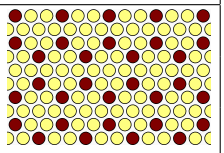
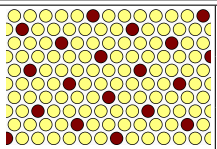
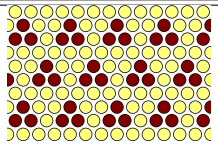
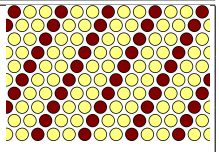
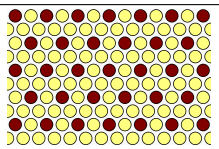
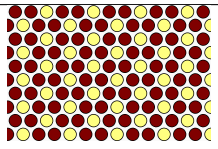
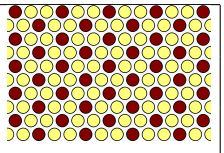
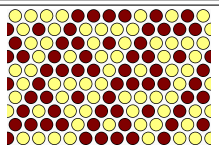
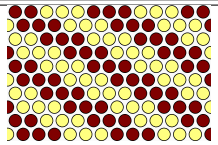
FLS	Ground State Crystal	FLS	Ground State Crystal a	Ground State Crystal b
$\{0\}$ 	$\mathcal{Z}=1$, $E_0=-1$, $g=1$ 	$\{23\}$ 	$\mathcal{Z}=9$, $E_0=-2/3$, $g=6$ 	$\mathcal{Z}=9$, $E_0=-2/3$ 
$\{1\}$ 	$\mathcal{Z}=7$, $E_0=-6/7$, $g=6$ 	$\{24\}$ 	$\mathcal{Z}=9$, $E_0=-2/3$, $g=6$ 	$\mathcal{Z}=3$, $E_0=-2/3$ 
$\{22\}$ 	$\mathcal{Z}=4$, $E_0=-3/4$, $g=3$ 	$\{31\}$ 	$\mathcal{Z}=3$, $E_0=-2/3$, $g=2$ 	$\mathcal{Z}=3$, $E_0=-2/3$ 
$\{32\}$ 	$\mathcal{Z}=20$, $E_0=-4/5$, $g=12$ 	$\{33\}$ 	$\mathcal{Z}=6$, $E_0=-2/3$, $g=6$ 	

FIG. 1: The groundstates for the 8 distinct FLS as defined in the text. The FLS are labeled as follow : the first digit of the name is the number of down spins (dark sites on the pictures), and the second one is the length of the longest sequence of up spins in the structure. Stuctures $\{06\}$ and $\{15\}$ will be named simply $\{0\}$ and $\{1\}$, without ambiguity. The geometrical multiplicity g of the FLS, number of sites in the unit cell $\mathcal{Z}$ and the energy per site E_0 in the groundstate are indicated. When two crystal states of same energy are known, we labeled as (a) the only one observed in simulations, apart for $\{31\}$ where both are observed.

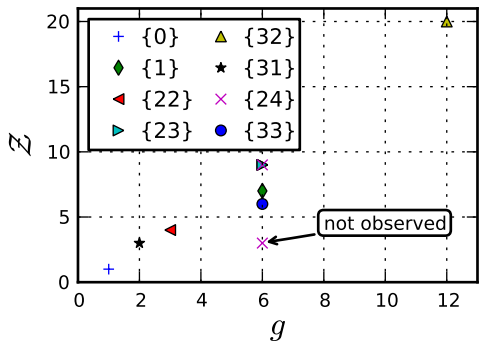


FIG. 2: The groundstate unit cell size Z plotted against the multiplicity g of the FLS for each of the 8 distinct local structures.

the FLS's achievable on the lattice. These are illustrated in Figure 1, along with their energy per site and unit cell size, for each choice of FLS. We find that the groundstates are all crystalline - a non-trivial result given the low symmetry of some of the local structures. In some cases we have found degenerate crystal groundstates, as indicated in Figure 1. In the case of $\{32\}$, there is a multiplicity of degenerate ground state structures arising from the sliding of the 'stripes' relative to one another. With the obvious exception of the $\{0\}$ structure, all groundstate energies are greater than -1, reflecting the frustration related to the inability of the favoured local structure to completely fill the available space. We note that the immediate consequence of this frustration is not to suppress crystallinity but rather to remove homogeneity in the groundstate, requiring instead that two or more different local environments be present even at the lowest possible energy. We also note the general trend indicated in Figure 2 that sees unit cell size increase $\sim$ linearly with the increasing number of distinct orienta-

tions of the FLS (listed in Figure 1 as the multiplicity g). We emphasize that there is no particular correlation between unit cell size and the energy of the groundstate, i.e. a low symmetry FLS is as likely to produce a stable crystal as is a high symmetry FLS.

We have carried out numerical simulations for each choice of FLS, using the Metropolis Monte Carlo algorithm due to Bortz et al [10] and employing periodic boundary conditions. A typical system size was 60×60 (the size was adjusted to accommodate the particular groundstate). In all cases, the lowest energy state obtained in the Monte Carlo simulations corresponded to the groundstate crystals identified in Figure 1. Of those FLS for which there were several distinct groundstate structures, i.e. the {23} and {24} systems, we found that they always freeze into a single crystal phase, crystals $23a$ and $24a$, respectively. The {31} system freezes into one of the two spin inversion symmetric structures $31a$ and $31b$. To follow the accumulation of order on cooling, we have plotted the average energy per site E against the temperature T in Figure 3 for four of the 8 choices of FLS. (A complete report is in preparation.)

We find striking variations between the different liquids related to how they accumulate order on cooling. Liquids {1} and {32}, for example, can achieve a density of FLS's corresponding to 90% of the crystal structure while remaining stable liquids. Others, such as {31} and {33}, achieve most of their local ordering as a phase transition. The order of the phase transition also appears to depend on the degree of ordering in the liquid. Where the order transition from the poorly ordered {31} liquid is 2nd order, we find 1st order transitions (as evidenced by the presence of hysteresis) for the more strongly ordering liquids, {33}, {24} and {1}. This trend resembles the scenario of the fluctuation-induced first order transitions discussed by Brazovskii [12] and Swift and Hohenberg [13]. Elsewhere [11], we shall present an explanation of this capacity of some liquids to accumulate a large amount of local order in terms of the different densities of states.

We find that the presence of local order in advance of crystallization correlates with the depression of the melting point with the transition temperature T_x, defined as the value of T at which the heat capacity exhibits a maximum. T_x decrease monotonically with decreasing energy of the liquid at the transition point. The accumulation of local order also results in a slowing down of relaxation and crystallization kinetics. While these two features - freezing point depression and slow kinetics - both suggest that the low energy liquids are likely candidates for glass formers, we have found crystallization still occurs quickly on supercooling these liquids and do not observe any long-lived metastablity when supercooled.

In should be acknowledged that the local order parameter represents a perfectly adequate order parameter for the freezing transition in a number of well studied simple liquids. An example of this is the well established use of the amplitude of spherical harmonics of the local coordination configurations in a liquids of Lennard-Jones particles as an order parameter for the formation of the face centred cubic crystal [14]. It was pointed out recently [1], however, that the appearance of local order can decouple from that of crystalline order when the unit cell of the crystal is significantly larger than the nearest neighbour coordination shell. The FLS lattice model provides a variety of ordering scenarios involving unit cells considerably larger than the individual site with which to examine the question of regarding the relationship between local and global order. To analyse this de-coupling we shall need two order parameters, one, ϕ_1, to measure local order and a second, ϕ_2, to quantify the degree of crystallinity. Let $\phi_1 = (E - E_\infty)/(E_o - E_\infty)$, where E_∞ and E_o are the high T limit and groundstate energies, respectively. The choice of crystalline order parameter will depend on the structure of the crystal. Here we shall make use of the simplicity of the crystals of the {1} and {31} FLS's which both take the form of hexagonal superlattices. For the {1} liquid, ϕ_2 is the probability that in any of the two possible hexagonal superlattices, an up spin will have 6 up spins as nearest neighbours. In order not to break the symmetry $up \leftrightarrow down$, the definition of ϕ_2 in the {31} liquid is modified to be the probability that a given site is surrounded by six neighbours of the same spin state in the superlattice. Both of these parameters represent the probability of an event that is unlikely in a random liquid and certain in a perfect crystal. The order parameter curves describing the route from liquid to crystal in the {1} and {31} systems are plotted in Figure 4. If local order could only appear as a consequence of crystallization (i.e. the strongly coupled case), we would expect the transition from liquid to crystal to correspond to a straight line of slope 1 in the (ϕ_1,ϕ_2) plane. We find that the {31} system comes close to this ideal while the ordering of the {1} system exhibits a strong deviation from the strong coupling limit. Remarkably, the latter manages to accumulate $\sim 80\%$ of the local order found in the crystal while exhibiting little to no trace of actual crystallinity. Can the different types of crystallization be directly correlated with the unit cell size of the crystal, as hinted at in ref. [1]? It is true that for the examples of ordering depicted in Figure 4, {1}, which exhibits a decoupling of local and crystalline order, has a larger unit cell than the {31} system ($Z = 7$ vs $Z = 3$). The correlation fails, however, for examples like the {33} liquid where the local order parameter remains a useful description of the crystallization transition despite a unit cell of 6 sites. While a large unit cell allows for the *possibility* of a decoupling between local and crystalline order, for the decoupling to actually occur requires that the local order can be accumulated while retaining sufficient entropy to stabilize the liquid against crystallization. We shall pursue this connection between entropy and local geometry

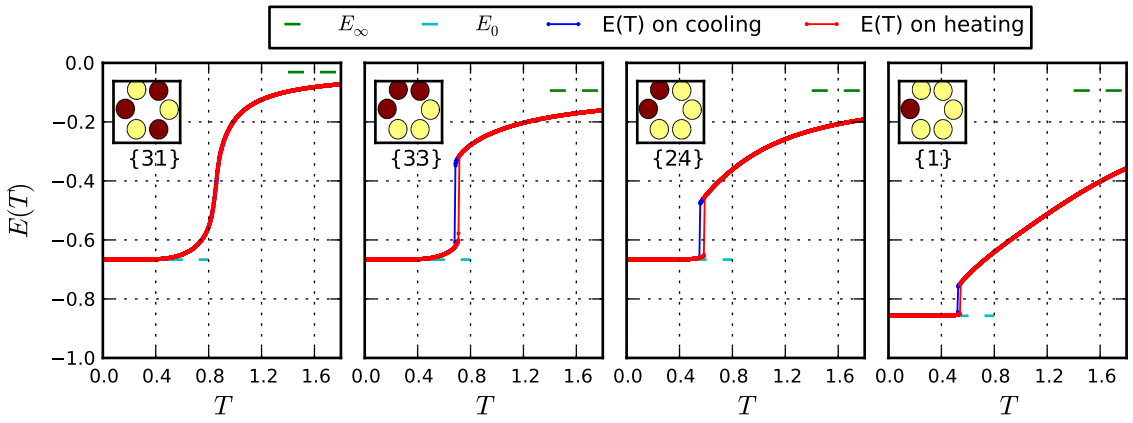


FIG. 3: Energy versus temperature curves for four FLS, from the seemingly continuous {31} structure for which all the accumulating structure is crystal-like to the first order {1}. These numerical data were obtained for long simulations, in an hysteresis cycle (cooling then heating) for systems of size around 60×60. In dashed lines are indicated the infinite temperature and ground state energies.

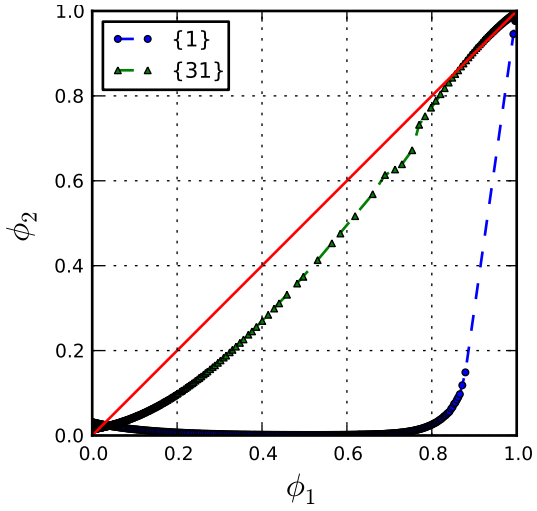


FIG. 4: The crystalline order parameter ϕ_2 (as described in the text) plotted against the local structure order parameter ϕ_1 for the {1} and {31} systems.

elsewhere [11].

In conclusion, we have introduced a new lattice model for liquids and crystals in which the favoured local structure is explicitly identified in the Hamiltonian and we have established the library of groundstates associated with the various choices of local structure. We find the groundstates to be crystalline, even for local structures with no symmetry (i.e. the {32} liquid). (This conclusion does not include the case where only a single enantiomer of the {32} FLS which will be treated elsewhere [11].) We have demonstrated a correlation between the decrease in local symmetry and the increase in the unit cell size of the global minimum. We also found no evidence of that low symmetry structures systematically produced high energy crystals. The most striking influence of the symmetry of the local structure was found, not in the crystal structure, but in the properties of the equilibrium liquid. Favoured local structures with high symmetry were found to undergo a crystallization transition from a liquid characterised by low density of favoured local structures. Liquids with low symmetry FLS's, in contrast, were generally able to accumulate more local order before crystallizing, their freezing points were depressed relative to the high symmetry liquids and the crystallization transition could not be properly described by reference to the local FLS order alone. The fundamental influence of the geometry of the local structure appears to be exerted through the multiplicity of collective structures it allows, thus determining the entropic cost incurred in accumulating local structure. Understanding this connection be-

tween local order and entropy in the liquid and its kinetic consequences are, we suggest, important problems to be addressed and we hope the FLS model, presented here, provides a useful tool in this regard.

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