Amorphous ground states and collective dynamics in a 2D glass-forming mixture

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Abstract. On cooling, many supercooled liquids arrive at a rigid disordered state, metastable to the crystal. In this paper, we characterize such amorphous ground states in a binary mixture of soft discs in 2D using molecular dynamics simulations. We find these ground states exhibit very strong correlations between local fivefold and sevenfold sites and an inherent stress heterogeneity. The heat capacity C_p is found to undergo an abrupt increase on heating through a glass transition temperature. We show that this increase is largely due to volume fluctuations.

1. Introduction

In a recent discussion of high temperature superconductivity, the comment was made that the problem was so hard that it could not *even* be simulated. The problem of the glass transition is not this hard. At least for simple liquids, we can reproduce most of the characteristic glassy phenomenology in computer simulations—at least over the six or seven orders of magnitude of time scales accessible to current computers. So how does this capability make the problem of understanding the complex cooperative dynamics easier?

   In this paper we shall examine the amorphous ground states and the thermal excitations of a binary mixture of soft discs in 2D using molecular dynamics simulations. To make our philosophical tack clear—we seek to develop a complete and explicit account of the collective processes responsible for the glassy behaviour of *one* 'simplest' model of a glass-forming liquid. We have established elsewhere [1, 2] that the 2D mixture reproduces all of the characteristic phenomenology of a fragile glass-forming liquid.

## 2. The model and the algorithm

We have carried out a series of constant pressure–constant temperature molecular dynamics (MD) simulations on a 2D system consisting of an equimolar mixture of two types of particle with diameters $\sigma_2 = 1.4$ and $\sigma_1 = 1$ and equal masses m. The three pairwise additive interactions are given by the purely repulsive soft-core potentials, $\varphi_{ab}(r) = \varepsilon[\sigma_{ab}/r]^{12}$, with $a, b = 1, 2$ and $\sigma_a = \sigma_{aa}$ and $\sigma_{12} = (\sigma_1 + \sigma_2)/2$. The cutoff radii of the interactions were chosen to be $4.5\sigma_{ab}$. The units of mass, length and time are m, σ_1 and $\sigma_1(m/\varepsilon)^{1/2}$ respectively. A total of $N = 1024$ particles were enclosed in a square box with periodic

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boundary conditions. The simulations were carried out at constant number of particles, pressure ($P^* = P\sigma_1^2/\varepsilon$) and temperature ($T^* = k_BT/\varepsilon$ where k_B is Boltzmann's constant) in which the instantaneous temperature and pressure are strict constants of the motion. The pressure was fixed at $P^* = 13.5$. For this pressure, the freezing temperature of single component 2D liquids of small and large particles are $T_f^* = 0.95$ and $T_f^* = 1.70$ respectively.

3. The complexity of the amorphous ground state

The behaviour of low temperature liquids is dominated by the presence of amorphous ground states. Understanding the origin and physically significant characteristics of these stable states represents the core problem posed by glassy behaviour. In this section we address the problem of characterizing the $T^* = 0$ ground states of the equimolar mixture.
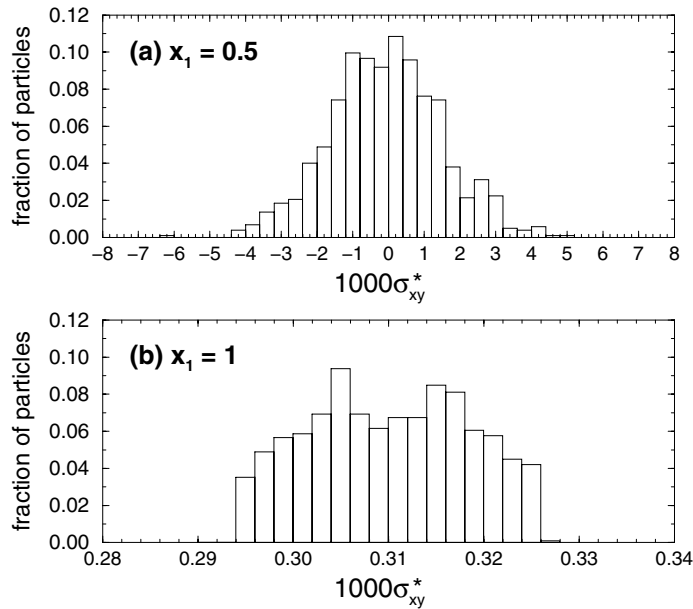
Figure 1. A comparison of the distribution of $T^* = 0$ shear stress σ_{xy} per particle in (a) the equimolar mixture and (b) a single component crystal of soft discs.

The mixture of soft discs with a diameter ratio of 1.4 has, at a reduced pressure $P^* = 13.5$, a eutectic point at $T^* = 0.7$ and a mole fraction of small particles of 0.8 [1]. Barring the possible stability of some more complicated crystal structures, the equilibrium phase below this temperature is coexisting randomly substituted crystals of large and small particles. Despite simulations runs of 10 times the structural relaxation time, no sign of demixing or crystallization has been observed in the equimolar mixture. Taking advantage of these long run times, we find little variation in the potential energy or density of amorphous ground states obtained from cooling different high temperature configurations. Significant quench rate dependence of the ground state was observed only for very rapid cooling rates [1].

The ground states exhibited no significant compositional segregation and no long range translational or orientational order [1]. The average shear modulus of these $T^* = 0$ amorphous states differs little from the high frequency modulus of the liquid [1]. We *have* identified two interesting features of the amorphous ground states which underline the complexity of these

stable states. First, analysing the topology of the structures using Voronoi polyhedrons, the ground states can be characterized as a network of tightly bound sequences of alternating fivefold and sevenfold sites. We have argued [1] that this close correlation has little to do with the asymptotic disclination-binding mechanism. The high disorder would curtail such elastic strain interactions. Instead, we propose that the statistics of dense packing of the mixtures compels the correlations. This correlation is noteworthy for its strength only. The fivefold and sevenfold sites themselves should not be thought of as 'defects'. They are, typically, quite stable features of the mixture packing. On heating the mixture, we find little correlation between the number of neighbours to a particle and the local relaxation time [2].

Of more direct physical significance, we find the amorphous ground states exhibit a broad distribution of local shear stress and pressure. In figure 1, the distribution of shear stress about the small particles in the mixture is compared with the stress distribution in the single component crystal. It is important to understand that this stress distribution is an unavoidable feature of the amorphous state and unrelaxable, except through crystallization. While we have yet to establish an explicit link between the stress distribution and glassy behaviour, we believe that amorphous stress is an important feature of the low temperature ground state. Alexander [3] has recently examined the contribution of such stress to the rigidity of disordered networks. Vitek and Egami [4] have reported local stress in excess of the bulk yield stress in models of amorphous alloys.

## 4. Thermal fluctuations and the anomaly in the heat capacity C_p

Given the complexity of the ground-state structure, we need to be able to separate out those structural features that we deem physically 'important'. In the context of the transition between glass and liquid, this means those ground-state features that are associated with the striking changes observed on heating.

The heat capacity C_p of the mixture exhibits a step-like anomaly at $T^* \approx 0.35$ in figure 2. (The thermal expansion coefficient shows a similar step while the isothermal compressibility does not.) Such an abrupt fall in the heat capacity at low temperatures is a common feature of glass formation. While it is typically attributed to falling out of equilibrium, we maintain that, in the case of the 2D mixture, the drop in C_p, at least down to $T^* = 0.4$, represents the equilibrium behaviour [1]. This claim is based on the fact that, down to this temperature, our averaging involves times considerably longer than the structural relaxation time. The enthalpy fluctuations, on which our calculation of C_p is based, can be resolved into fluctuations in potential energy, volume and the cross-correlation. As shown in figure 2, C_p is dominated by volume fluctuations. This peak corresponds to a faster than quadratic increase of $\langle \Delta V^2 \rangle$ with respect to temperature.

What kinds of motion drive these volume fluctuations? The correlation time for these volume fluctuations is found to be very short, roughly that of a single collision time for all temperatures. We have, so far, been unable to find any evidence of slow collective fluctuations resembling intermittent 'jumps' between distinct stable configurations of an energy 'landscape' making significant contributions to the peak in C_p.

5. Conclusion

The main results of this paper have been to identify structural, mechanical and thermal features of the amorphous ground states of the 2D binary mixture that differentiate these rigid states from the crystalline ground state. The strong correlation between fivefold and sevenfold sites is an
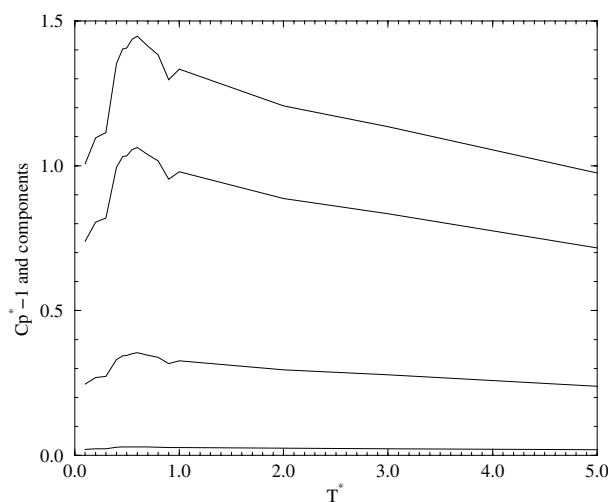
Figure 2. The reduced heat capacity at constant pressure C_p minus the kinetic energy fluctuations (upper curve) as a function of T^* in the equimolar mixture. The three contributions to this quantity from energy (U) and volume (V) fluctuations are shown as the three lower curves. In order of decreasing magnitude, these contributions are $NP^{*2}\langle \Delta V^2 \rangle / T^{*2}$, $2NP^*\langle \Delta V \Delta U \rangle / T^{*2}$ and $N\langle \Delta U^2 \rangle / T^{*2}$, where P^* and T^* are the reduced pressure and temperature.

aspect of the dense packing of mixed discs that may provide a structural signature of the arrested state. The consequences of the broad distribution of shear stress and pressure in the amorphous states remain to be explored. Can this local strain energy be transferred to collective processes in the glass? The question of collective excitations is brought into sharp focus with the step in C_p at $T^* \approx 0.35$. Given the significance of volume fluctuations we expect $C_p > C_V$. (This, of course, is trivially true in the extreme case of hard discs for which $C_V = 0$.) That this difference persists down to the lowest temperatures is contrary to the standard assumption that $C_p \approx C_V$ for solids. The absence of any extended memory in volume fluctuations as we cool through the glass transition raises the possibility that enthalpy fluctuations are dominated by rather rapid dynamics—i.e. with respect to the landscape picture, oscillations within a potential well rather than hopping between different wells. Clearly, other characteristic glassy phenomenologies such as slow structural relaxation and diffusion *do* depend intimately on collective processes. Perhaps the glass transition of this fragile liquid may consist of a collection of transitions, bound together within a narrow temperature range by the abrupt loss of interparticle coupling on heating. Current work aims to understand whether the heterogeneities of the ground-state structure play an important role in these thermal fluctuations.

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