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Stalking the collective process: establishing a dialogue between simulation and speculation

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Abstract. It is now well established that molecular dynamics simulations realistically capture the onset of glassy behaviour in simple liquids. Despite the extensive information with which these models can, provide us concerning the cooperative fluctuations responsible for the special properties of glass-forming liquids, the literature remains dominated by the same speculative models that characterized the field 20 years ago. The difficulty in exploiting simulations lies in articulating questions concerning cooperative behaviour in forms explicit enough to be addressed by the calculations. This difficulty will be discussed in the context of dynamic heterogeneities, subdiffusive behaviour and anomalous heat capacities in simulations of a glass-forming mixture.

1. Introduction

The starting point of this paper is the assertion that much of the characteristic phenomenology of glass formers can now be reproduced in molecular dynamics simulations of simple model liquids. In presenting an unrestricted access to microscopic information about the structure and dynamics associated with relaxation in supercooled liquids, we are left with one remaining obstacle to a satisfactory resolution of ‘the glass problem’. That obstacle is our own difficulty in articulating the ‘problem’ in a form explicit enough for a computer to answer. Irrespective of one’s views on the physical relevance of the various model liquids currently under study, it seems difficult to avoid the conclusion that if you cannot pose your glass question in a ‘computer answerable’ form (at least by an idealized supercomputer) then you are unlikely to be able to answer it by any other means.

The challenge then is to devise answerable questions concerning the relationship between glassy phenomenology and particle configurations and dynamics. One strategy is to speculate the existence of a certain kind of microscopic feature (structural or kinetic) and deduce the resulting phenomenology. The literature on glasses has many examples of this approach. There are two problems here. As the same phenomenology may be reached from many different starting assumptions, success in this programme does not allow one to conclude that the starting speculation is correct, merely that it is not demonstrably wrong. Second, speculations on cooperative processes among particles are often too vague as to be subject to direct testing by simulations.

In this paper we shall examine the alternate route to establishing relationships between phenomenology and particle dynamics in which we use simulations to work *from* the phenomenology towards the microscopic degrees of freedom. As glasses are defined by their phenomenology rather than any formal criteria, this approach has a certain logical advantage over the traditional approach described above. The challenge of this ‘hunt’ is to

retain clear connection between the meso- or microscopic degrees of freedom being studied and the macroscopic behaviour of ultimate interest. The model system used in this work is a binary mixture of soft discs in 2D. We have established [1, 2] that the 2D mixture reproduces all of the characteristic phenomenology of a fragile glass-forming liquid. In sections 3, 4 and 5 we review efforts to trace the microscopic origin of the slowing down and stretching of structural relaxation with cooling. In section 6 we describe progress on the origin of the anomalous heat capacity at the glass transition.

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 similar system has been studied by Muranaka and Hiwatari [3] and, under nonequilibrium conditions, by Yamamoto and Onuki [4]. A total of $N = 1024$ particles were enclosed in a square box with periodic boundary conditions. The simulations were carried out at constant number of particles, pressure ($P^* = P\sigma_1^2/\varepsilon$) and temperature ($T^* = k_B T/\varepsilon$ where k_B is Boltzmann's constant), using the constraint MD algorithm of Evans and Morriss [5] 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 heterogeneity of dynamics

Starting from an observed relaxation spectrum, it is relatively straightforward to ask how this dynamics is distributed over the individual particles. In the vicinity of the onset of rigidity, supercooled liquids exhibit a broadening of the distribution of the local relaxation kinetics [2]. A visual sample of these collective fluctuations is provided by the map of displacements presented in figure 1. The lines represent the displacement of each particle between the position it occupies following a conjugate gradient quench of the initial configuration to a potential energy minimum and the position it occupies following a similar quench of the final configuration 100τ later. The trajectory was run at $T^* = 0.4$. Two kinds of motion are visible. A small number of particles have undergone large displacements. These motions all involve some kind of collective entrainment, either as strings or closed loops. Associated with these large displacements is what appears to be a complex strain field extending through the surrounding particles. Such figures underline both the large spatial variations in the local relaxation kinetics and the coupling of these local anharmonicities via strains of the intervening 'immobile' regions.

Given that the existence of dynamic heterogeneities in supercooled liquids is now generally accepted, what should we do with them? First, what can dynamic heterogeneities tell us of their own origin, i.e. the underlying structural and dynamic reasons for these spatial fluctuations? We address this question in section 4. A second question: are dynamic heterogeneities a core feature of glassy dynamics or just some interesting but secondary fluctuations riding on the back of the underlying glass transition? There appears to be growing evidence that dynamic heterogeneities are essential to properly account for the broadening of the relaxation

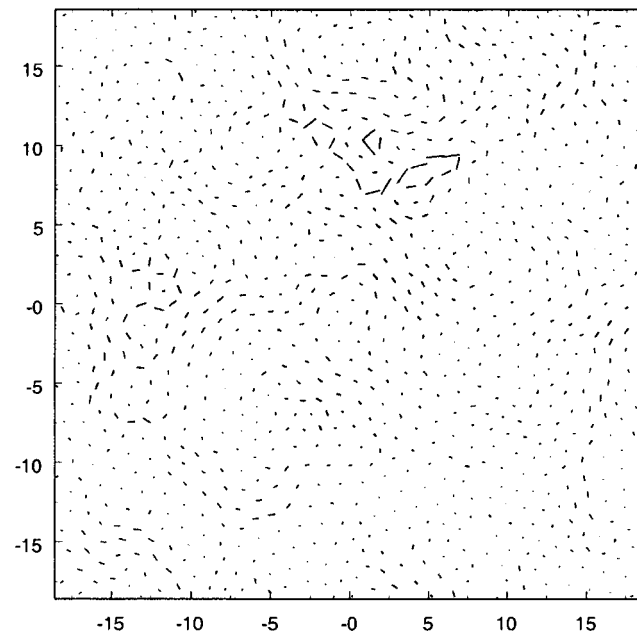


Figure 1. The line segments indicate the particle displacements between two potential energy minima generated by performing conjugate gradient quenches on $T^* = 0.4$ configurations separated by 100τ .

spectrum on supercooling. To the extent that this feature is seen as a basic aspect of glassy phenomenology, heterogeneities would appear to be a central element of the problem. This conclusion raises an interesting question for mean field theories [6, 7] of the glass transition which, to date, has received little attention. Having neglected fluctuations, what aspects of the collective dynamics *do* they describe?

4. Correlations between dynamic and structural fluctuations

What can the fluctuations in local dynamics tell us about correlations between structure and dynamics? Is there a feature of a single configuration that distinguishes slow particles from fast ones? The recent literature offers a range of answers to this question, the difference hinging on what is meant by ‘distinguishes’. A number of workers [8, 9] have noted that there is a correlation between a particle having a high or low potential energy and it being identified as a fast or slow particle, respectively. Potential energy fluctuations have been identified as the origin of dynamic heterogeneities on the basis of this observed correlation [9]. We have argued [2] that the observed correlations are insufficient evidence for this kind of strong causal connection. We have examined the correlation between local hexagonal order and relaxation times [2]. While the average hexagonal order in the slow populations is slightly higher than that in the fast population (see figure 2), the distributions of structure are almost an order of magnitude greater than the difference in means. (A particle’s relaxation time is defined as the first passage time for a particle to move a distance $|r^*| = 1.0$. The definition of local hexagonal order is given in the caption of figure 2.) The large widths of these distributions mean that, despite the correlation between mean relaxation time and mean hexagonal order, local structure is of little use in predicting local relaxation time. On this basis it would seem

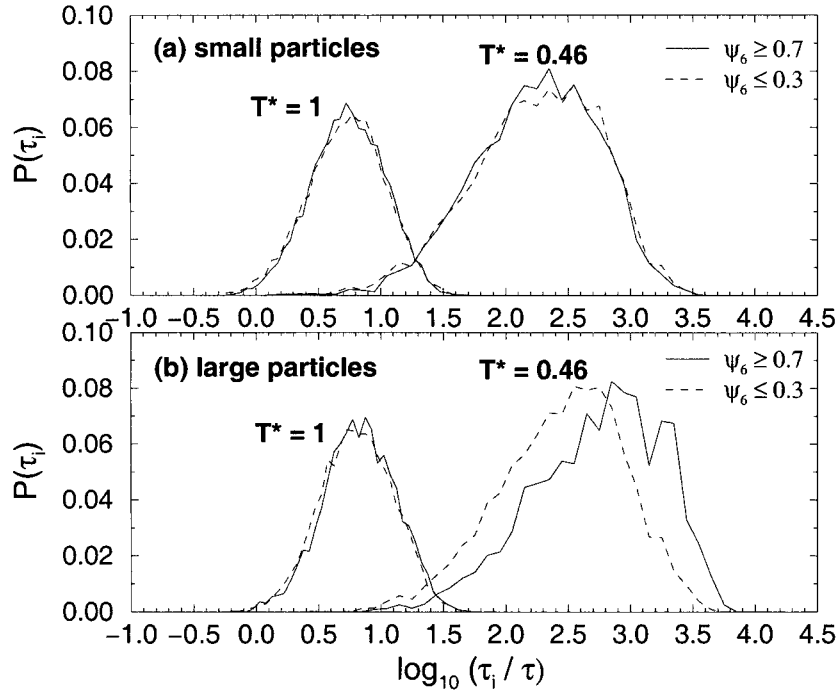


Figure 2. Plots of the distribution of local relaxation times $P(\tau)$ for the small and large particles that have high ($\psi_6 \geq 0.7$) and low ($\psi_6 \leq 0.3$) local ordering at $T^* = 1.0$ and 0.46 . The hexagonal order parameter $\Psi_6(i)$ at particle i is defined as

$$\Psi_6(i) = \frac{1}{n_i} \sum_{j=1}^{n_i} \sum_{k=1}^{n_i} \cos 6\theta_{ij,ik}$$

where n_i is the number of nearest neighbours around particle i and $\theta_{ij,ik}$ is the angle between the vectors \mathbf{r}_{ij} and \mathbf{r}_{ik} where particle j and k are nearest neighbours of particle i .

difficult to support a claim that local structural fluctuations are the ‘origin’ of the dynamic heterogeneities. Similarly broad distributions have been observed with respect to potential energy [8]. Clearly these are just the preliminary attempts to find correlations between local configurational properties and local dynamics. It is, however, quite possible that dynamics reflects a complicated *nonlocal* dependence on structure. Given the extended chains of particle movements depicted in figure 1, it seems likely that whether or not a particle undergoes a large displacement may be determined by the environment of a distant particle in the chain.

5. Extended velocity correlations near the onset of rigidity

Let us pursue further the coexistence of solid-like and liquid-like motion as the glass transition is approached. It is a commonplace observation that, as the supercooling increases, so to does the time interval required before the mean squared particle displacement $\langle \Delta r^2 \rangle$ exhibits the linear time dependence characteristic of diffusion. We find [10] that $d\langle \Delta r^2 \rangle / dt$ can be reasonably described by a power law decay $t^{-\eta}$ in this crossover time interval with $0.5 < \eta < 0.9$ in the temperature domain over which the power law applies. Since

$$\frac{d\langle \Delta r^2 \rangle}{dt} = 2 \int_0^t dt' \langle v(0)v(t') \rangle$$

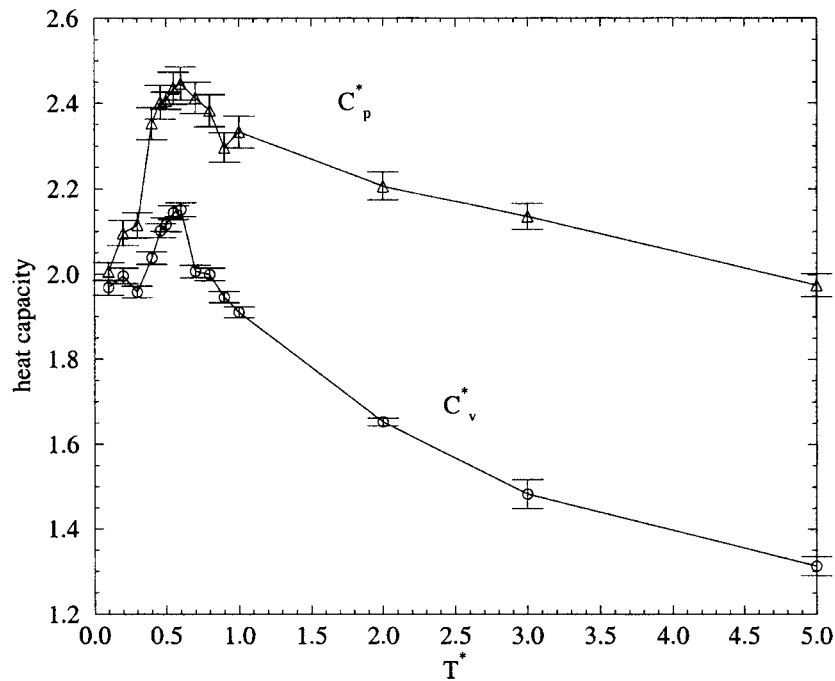


Figure 3. The reduced heat capacities C_P and C_V per particle as a function of temperature. The constant volume simulations were done at a volume equal to the average volume from the constant pressure calculations at that same temperature.

the existence of this extended decay of $d\langle\Delta r^2\rangle/dt$ implies the existence of a long negative tail in the velocity autocorrelation function of the form $-t^{-(\eta+1)}$ over the same intermediate time interval associated with β relaxation. The physical origin of this velocity memory and its connection with the incipient rigidity poses a fascinating question. We have considered the following simple model of the velocity autocorrelation over this intermediate time [10]. The probe particle is assumed to be embedded in a cluster of harmonically bound particles whose dynamics are subject to damping. Over a range of cluster size and friction coefficients we find an extended negative region to the velocity autocorrelation of our probe particle which decays with a power law similar to that observed in the liquid simulations.

6. Thermal fluctuations and the anomaly in the heat capacity C_P

While relaxation dynamics occupies much of the focus in glassy studies, changes in heat capacity as one cools through the glass transition remain the most widely used signature of this transition. The heat capacity C_P at constant pressure of the 2D mixture, shown in figure 3, exhibits a steplike anomaly at $T^* \approx 0.35$ [1]. 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. C_P , it turns

out, is dominated by volume fluctuations. Does this mean that C_V , the heat capacity at constant volume, will show no glassy anomaly? We have calculated C_V at the same temperatures and average volumes as used to calculate C_P . The results, shown in figure 3, indicate that the glassy anomaly persists in C_V , albeit with reduced amplitude. The residual difference between C_P and C_V below the glass transition (i.e. $T^* \approx 0.35$) indicates that the glass retains a significant thermal expansion coefficient, unlike a harmonic solid. In fact, we find a steplike increase in the thermal expansion coefficient coincident with that seen in C_P .

The demonstration that C_V exhibits a significant glassy anomaly could be an important step in tracing its molecular origin. While the enthalpy fluctuations in C_P contain an unavoidably global character, the energy fluctuations responsible for C_V can be reduced to the contributions of individual degrees of freedom (i.e. particles or modes). We are currently looking at a number of strategies for identifying the contributions to C_V of various cooperative fluctuations. Stillinger and Debenedetti [11] have concluded that thermal expansivity for particles interacting via inverse power law repulsions is dominated by vibrational motion about individual potential energy minima as opposed to fluctuations between different minima. The distinction between a strongly anharmonic vibration and an actual barrier crossing in terms of contributions to C_V is a particular question of interest.

7. Conclusion

The strategy, outlined in this paper, of using simulations to trace glassy phenomenology back to degrees of freedom with increasing amounts of microscopic detail has yet to arrive at a satisfactory 'final answer' concerning the origins of either the glassy relaxation spectrum or the heat capacity anomaly. While it is clear that diffusion at low temperatures proceeds by 'soft' localized excitations involving strings or loops of some ten particles, much remains to be understood. Are there structural signatures of these soft modes? What role do they play in structural relaxation and in the heat capacity? Computer simulations provide us with perhaps the most viable prospect, not only of answering these questions, but of even asking them.

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