

Chapter 8

Final Discussion

In this thesis we have sought to provide a clearer picture of the relationship between structure and dynamics in supercooled liquids and glasses. We have developed new methods for investigating this relationship at a microscopic spatial level, and have applied these to the study of a two-dimensional glass-forming alloy. We have also characterised the phase behaviour, and structural and dynamic properties, of several related model alloys, thereby laying the foundations for a rich extension of the former work. Our results firmly portray the glass transition as a continuous transition from structure-independent dynamics to structure-dependent dynamics.

In Part I, we investigated the role of structure in the development of spatially heterogeneous dynamics in a supercooled random alloy. Specifically, a binary soft-disc mixture with additive interparticle potential was studied. New tools were conceived - the isoconfigurational ensemble, dynamic propensity, the single particle non-Gaussian function, and the single-particle Debye-Waller factor - and used to obtain the clearest picture yet of the relationship between structure and dynamics in a glass-forming liquid.

By considering the set of N -particle trajectories through a configuration, i.e. an isoconfigurational ensemble, we were able to study the effect of structure on dynamics at a microscopic level without the additional noise of momenta fluctuations. We found that over the isoconfigurational ensemble, some particles are on average more mobile than others, i.e. some particles have a higher susceptibility to motion than others. We studied this susceptibility on both the structural relaxation time - using the dynamic propensity, and on the timescale of the secondary β -relaxation - using the single particle Debye-Waller factor (DW factor).

As the random alloy is supercooled, structural variations become increasingly important for dynamics and ultimately cause relaxation times to vary by orders of magnitude from one region of the supercooled liquid to another. This was evidenced by the rapid increase in the variance and range of the propensity distribution upon supercooling, and the increasing clustering of particles with similar mobility. It also strongly suggests that the various properties of supercooled liquids that have been attributed to the appearance of spatially heterogeneous dynamics - such as the breakdown of scaling between translational and rotational diffusion, the appearance of non-Fickian transport, and the dependence of T_g on film thickness in polymer films - depend upon fluctuations in the structure of the liquid. If this is true, it places increased importance on understanding the structure of supercooled liquids and glasses, and in particular the spatial variation in structure, not just for understanding the stability of glass-formers to crystallisation, but also for understanding their macroscopic properties.

Upon supercooling, the variability of the individual particle motion also increases rapidly. Even the most susceptible regions become capable of ‘sticking’ in a given run, and when they do ‘slip’ the mobile particles move far from their initial positions. The individual particle displacements become increasingly non-Gaussian and the system dynamics becomes increasingly intermittent in character. This suggests a hierarchy of structural domains, from marginally jammed to overconstrained.

In Chapter 3 we demonstrated that the spatial heterogeneity of the single particle DW factor - a dynamic measure of structural ‘looseness’ - was able to predict the coarse-grained spatial variation in dynamic propensity. This provides a link - via the initial configuration - between dynamics occurring before and during the α -relaxation over timescales separated by two orders of magnitude. Given the subtlety of the collective mechanical constraints probed by the short-time dynamics, the DW factor should provide an upper bound on what one can hope to predict from any measure of the initial configuration.

While the present work has not looked at the effect of structure on dynamics below T_g , the results just described suggest that previous observations of spatial heterogeneity in vibrational motion below T_g are also likely to be due to spatial variations in structure. This therefore suggests a continuous relationship between spatial variations in structure and dynamics extending from below T_g up to the normal liquid regime.

We also found that the spatial distribution of DW factors changes substantially on the timescale of the β process. This implies that the susceptibility of the ‘loosest’ particles changes rapidly. It also makes the spatial correlation between the DW factor and the propensity all the more surprising. The answer is that although parts of the initial configuration change susceptibility very rapidly, other parts relax much slower and still influence the dynamics on much longer timescales. Thus, although the DW distribution changes rapidly the hot spots for short-time motion are mostly confined to the larger high propensity region(s) over much longer timescales. This appears to be supported by a comparison of the time series of DW maps with the propensity distribution for the configuration used as a starting point of the time series (in Chapter 3).

The local free volume, local potential energy and local coordination environment all fail to predict the spatial variation in dynamic propensity or the DW factor, even upon coarse-graining of the free volume and potential energy. This indicates that simple isotropic measures of structure are unable to capture the microscopic details of how structure affects dynamics. It appears that some more complicated - perhaps anisotropic - aspect of the particle packing is responsible for determining the dynamic susceptibility of different domains. The best defined regions - in terms of their effect on mobility - are the clusters of L06 environments which almost universally have low propensity and DW factors. We conclude that the heterogeneous effect of structure on dynamics, as characterised by the spatial variation in propensity, is due to a combination of overconstrained regions which consist mainly of distinct structural entities (large particle crystallites), and marginally constrained regions which have less well-defined structures. The latter are sufficiently constrained to prevent motion but are easily made mobile with an appropriate momenta fluctuation.

These results have a number of implications for various conceptual pictures of supercooled liquid dynamics. The failure of geometric free volume to predict the spatial variation in both the propensity and the DW factor, even after coarse-graining, casts doubt on the microscopic basis of theories of the glass transition based purely on free volume, and highlights the importance of testing whether correlations between macroscopic quantities persist at a microscopic level. The rapid changes that occur in the spatial distribution of the DW factor also demonstrate that a simple picture of defect diffusion is unable to account for the effect of structure on dynamics in this glass-former. Whatever property of the structure that causes one region of the

sample to be more mobile than another is able to be transferred from one region to another with little movement of the intervening particles. Finally, we note that the spatial distribution of propensity is essentially the starting point for several models of glass relaxation such as the facilitated spin models and the cooperative lattice gas models. The failure of simple structural measures to predict the spatial distribution of propensity bears a mixed message for programs in which atomic models of glass-formers are mapped onto spin models through an appropriate spatial coarse-graining of the former. Our results suggest that finding this appropriate spatial averaging to capture the subtle nonlocal character of particle constraints is a highly nontrivial task. On the other hand, our results certainly support the proposition that the initial pattern of local facilitation, as measured by the short-time dynamics, governs much of the subsequent heterogeneous dynamics.

In Part II, we investigated the effect of varying the interparticle potential on the phase behaviour of this glass-former. The structural and dynamic properties of six new systems were characterised, thus substantially adding to previous knowledge of crystallisation and glass-formation in binary soft-disc mixtures. The results provide a sense of the generality of the picture described above, and have laid the foundations for a rich extension of the former work.

When the interparticle potential σ_{12} is made greater than additive, there is an effective repulsion between unlike particle species and phase separation occurs upon cooling. On the other hand, when σ_{12} is decreased from additive there is an effective attraction between unlike particle species and the asymmetric H2 and symmetric S1 substitutionally ordered crystals are stabilised at equimolar composition. Interestingly, at non-equimolar compositions amorphous solids are formed on cooling. Together with the mixture studied in Part I, these form a complete structural range of alloy glasses, from random alloy to chemically ordered. As the degree of chemical ordering increases, the number of dominant local environments decreases, the structure becomes more homogeneous, and the medium-range order becomes more defined. Thus, we find that small changes to the interparticle potential stabilise amorphous solids with substantially different structures. The structures of the glass-formers also differ with respect to the amount of crystalline order that they have. The random alloy has substantial regions of large particle crystallites (the X_L phase), while the glass-former with $\sigma_{12} = 1.1$ shows very little sign of X_L or H2 crystalline environments. The glass-former with $\sigma_{12} = 1.0$, studied in Chapter 5, is also intriguing,

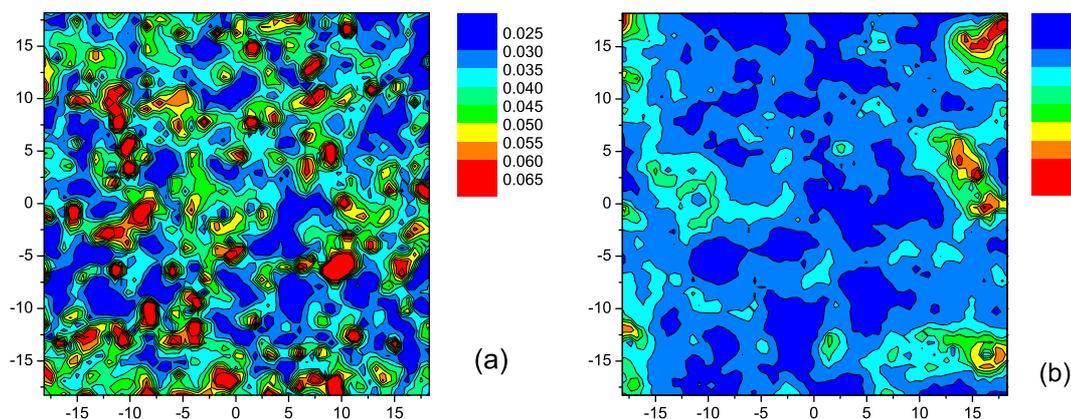


Figure 8.1: Contour plots of the spatial distribution of particle Debye-Waller factors for configurations at $T = 0.4$ for the system with (a) $\sigma_{12} = 1.1$, $x_1 = 0.3167$ and (b) $\sigma_{12} = 1.2$, $x_1 = 0.5$. The DW factors were calculated using 100 runs of 10τ duration each. Note the substantial difference in the spatial distribution of mobility. Different colour scales were used to enhance this difference.

because it appears to be as close to an ideal glass as one could hope to get. It is a particulate model, in which glass-formation arises naturally, without the need for ad-hoc model building; its low-temperature structure can be concisely described as a random tiling with defects, with most particles finding themselves in just five distinct environments; and videos of its low-temperature dynamics suggest that it is dominated by defect motion. (So perhaps defect diffusion models are appropriate for some glasses, namely those with strong chemical ordering.) The potentially soluble nature of the 1.0 glass-former also raises an interesting question: given a complete theoretical model of the glass transition, what next?

As we have already described, the presence of large particle crystallites in the random alloy glass-former has a significant impact on its dynamic properties. It should therefore be insightful to repeat the isoconfigurational analysis for these new glass-formers and compare the results to those obtained for the random alloy. As an example, in Figure 8.1 we compare the spatial distribution of structural ‘looseness’ for the non-additive system with $\sigma_{12} = 1.1$, and for the additive glass-former studied in Part I. Both plots are for configurations at $T = 0.4$, at which temperature the structural relaxation times for the two systems are similar. Note that the non-additive glass-former, which has the more homogeneous structure, also has a more homogeneous distribution of mobility, in the sense that particles with similar mobility are

less clustered. The range between high and low mobility is roughly the same for both systems.

The results just described raise a number of questions. Does the effect of structure on particle motion vary significantly between different glass-formers, as the plots in Figure 8.1 suggest? To what extent does the type and quantity of higher-symmetry local and medium-range order affect the properties - such as strength, conductivity and stability to crystallisation - of the glass-former? And how does the relationship between structure and dynamics differ in strong liquids, in non-alloy glasses, and in 3D glass-formers?

In conclusion, our results describe the increasing influence of structure on dynamics during the glass transition. In particular, the development of heterogeneity in the spatial distribution of dynamic propensity for a fragile glass-former demonstrates that structural variations can have a significant impact on relaxation in supercooled liquids. The isoconfigurational ensemble method provides a real-space picture of this transition from structure-independent to structure-dependent dynamics, that is complementary to the configuration-space perspective of the energy landscape view of glass-formation. It also has the additional benefit of providing the means to test for the presence of spatial correlations between structural and dynamic quantities on a microscopic spatial level. As the work in this thesis has demonstrated, this is an important test for distinguishing between those correlations that exist only at the bulk level and those that also operate at the microscopic level. Only the latter can provide insight into the detailed structural dependence of material properties.