Structure and Dynamics in Two-Dimensional Glass-Forming Alloys

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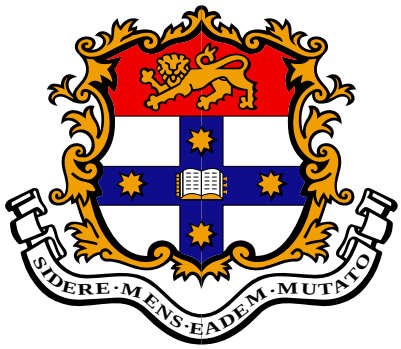
of the requirements for the degree of
Doctor of Philosophy



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Abstract

The glass-transition traverses continuously from liquid to solid behaviour, yet the role of structure in this large and gradual dynamic transition is poorly understood. This thesis presents a theoretical study of the relationship between structure and dynamics in two-dimensional glass-forming alloys, and provides new tools and real-space insight into the relationship at a microscopic level.

The work is divided into two parts. Part I is concerned with the role of structure in the appearance of spatially heterogeneous dynamics in a supercooled glass-forming liquid. The isoconfigurational ensemble method is introduced as a general tool for analysing the effect that a configuration has on the subsequent particle motion, and the dynamic propensity is presented as the aspect of structural relaxation that can be directly related to microscopic variations in the structure. As the temperature is reduced, the spatial distribution of dynamic propensity becomes increasingly heterogeneous. This provides the first direct evidence that the development of spatially heterogeneous dynamics in a fragile glass-former is related to spatial variations in the structure. The individual particle motion also changes from Gaussian to non-Gaussian as the temperature is reduced, i.e. the configuration expresses its character more and more intermittently.

The ability of several common measures of structure and a measure of structural 'looseness' to predict the spatial distribution of dynamic propensity are then tested. While the local coordination environment, local potential energy, and local free volume show some correlation with propensity, they are unable to predict its spatial variation. Simple coarse-graining does not help either. These results cast doubt on the microscopic basis of theories of the glass transition that are based purely on concepts of free volume or local potential energy. In sharp contrast, a dynamic measure of structural 'looseness' - an isoconfigurational single-particle Debye-Waller (DW) factor - is able to predict the spatial distribution of propensity in the supercooled liquid. This provides the first microscopic evidence for previous correlations

found between short- and long-time dynamics in supercooled liquids. The spatial distribution of the DW factor changes rapidly in the supercooled liquid and suggests a picture of structural relaxation that is inconsistent with simple defect diffusion. Overall, the work presented in Part I provides a *real-space* description of the transition from structure-independent to structure-dependent dynamics, that is complementary to the configuration-space description provided by the energy landscape picture of the glass transition.

In Part II, an investigation is presented into the effect of varying the interparticle potential on the phase behaviour of the binary soft-disc model. This represents a different approach to studying the role of structure in glass-formation, and suggests many interesting directions for future work. The structural and dynamic properties of six different systems are characterised, and some comparisons are made between them. A wide range of alloy-like structures are formed, including substitutionally ordered crystals, amorphous solids, and multiphase materials. Approximate phase diagrams show that glass-formation generally occurs between competing higher symmetry structures. This work identifies two new glass-forming systems with effective chemical ordering and substantially different short- and medium-range structure compared to the glass-former studied in Part I. These represent ideal candidates for extending the study presented in Part I. There also appears to be a close connection between quasicrystal- and glass-formation in 2D via random-tiling like structures. This may help explain the experimental observation that quasicrystals sometimes vitrify on heating. The alignment of asymmetric unit cells is found to be the rate-limiting step in the crystal nucleation and growth of a substitutionally ordered crystal, and another system shows amorphous-crystal coexistence and appears highly stable to complete phase separation.

The generality of these results and their implications for theoretical descriptions of the glass transition are also discussed.

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Publications

Most of the work presented in Part I of this thesis has been published or submitted for publication, and it is anticipated that much of the work presented in Part II will also be published. The chapters and corresponding publications are as follows:

Chapter 2:

- "How Reproducible is the Structure of Dynamic Heterogeneities in Glass-Forming Liquids?", Widmer-Cooper, A., Harrowell, P., *AIP Conference Proceedings* **708**, 711 (2004).
- "How Reproducible are Dynamic Heterogeneities in a Supercooled Liquid?", Widmer-Cooper, A., Harrowell, P., Fyneweaver, H., *Phys. Rev. Lett.* **93**, 135701 (2004).
- "On the Study of Collective Dynamics in Supercooled Liquids through the Statistics of the Iso-Configurational Ensemble", Widmer-Cooper, A., Harrowell, P., *submitted for publication* (2006).

Chapter 3:

- "On the Relationship Between Structure and Dynamics in a Supercooled Liquid", Widmer-Cooper, A., Harrowell, P., *J. Phys. Condens. Matter*, **17** S4025 (2005).
- "Free Volume cannot Explain the Spatial Distribution of Debye-Waller Factors in a Glass-Forming Binary Alloy", Widmer-Cooper, A., Harrowell, P., *J. Non-Cryst. Solids*, **352**, 5098 (2006).
- "Predicting the Long-Time Dynamic Heterogeneity in a Supercooled Liquid on the Basis of Short-Time Heterogeneities", Widmer-Cooper, A., Harrowell, P., *Phys. Rev. Lett.*, **96**, 185701 (2006).

We shall not cease from exploration
And the end of all our exploring
Will be to arrive where we started
And know the place for the first time.

From ‘Little Gidding’, by T. S. Eliot (1888–1965)

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