Chapter 1

Introduction

We introduce the study of amorphous solids and glass-formation and emphasise the importance of a structural underpinning for any complete description of this transition. The aim of the thesis is also established in relation to recent experimental work on glass-formers and amorphous alloys.

1.1 What is the Role of Structure in the Glass Transition?

Glasses and the glass transition represent, in the much quoted estimate of a Nobel laureate, "perhaps the deepest and most interesting unsolved problem in condensed matter physics" [1]. Glass-forming materials have also become an integral part of our lives, from plastics to building facades, food storage, health science and the rewritable CD; and the recent discovery of bulk metallic glasses looks set to greatly increase the range of applications. However, a detailed understanding of the connection between structure and dynamics in these materials, and in glass-formers in general, is lacking. We believe that this knowledge is necessary for any complete theoretical description of the glass transition, and will likely aid in the engineering of such materials for specific applications. As Cahn [2] has argued, it is generally the ability to make a strong link between microscopic structure and physical properties that essentially defines an established field of material science.

It has been known for centuries that if a liquid is quenched sufficiently fast, it can be cooled below its melting/freezing point T_m without crystallising. Below T_m, the fluid is called a supercooled liquid. With continued cooling its viscosity increases rapidly until eventually viscous flow ceases on the timescale of a typical experiment. At lower temperatures the structural relaxation time can be years or longer. The glassy state is a true solid, as the shattering of a mirror demonstrates. However, despite its rigidity, mechanical strength and elastic properties, the microscopic structure of a glass lacks any form of long-range order, thus distinguishing it from crystalline solids. For this reason, the term *amorphous solid* is often used synonymously with glass. The glassy state is sometimes incorrectly assumed to have the same structure as a liquid. While there is no development of long-range order, there are some changes in local and medium range ordering which, as we demonstrate in this thesis, become significant as the glass-forming liquid is supercooled.

The continuous transition from the liquid to solid state associated with the glass transition presents a number of puzzles with respect to the role of structure: (i) how does structure change to cause a continuous transition from fluid liquid to rigid solid? (ii) what is responsible for the rigidity of the glassy state? and (iii) how do preferred higher-symmetry structures influence the properties of the glass-former and its stability to crystallisation? While the precise structural details will vary from material to material, the broad phenomenology common to all glass-formers suggests that some aspects of the relationship between structure and dynamics are universal.

Experimental probes of structure in the supercooled liquid and glassy states generally return information on the average structure about particles in the form of the structure factor - from X-ray and neutron scattering - and the pair distribution function that can be derived from it. As these show only small changes, most experimental work on glasses has focused on studying the large changes in dynamic properties and unusual dynamic behaviour associated with the glass transition, and on finding correlations between various dynamic properties of glass-forming liquids. It has been largely left to theoreticians to address the role of structure in glass-formation, often involving the study of simple model systems. In this thesis we use molecular dynamics to investigate the relationship between dynamics and structure in a family of binary soft-disc mixtures that form 2D analogues of many of the structures observed in alloys. We discuss our choice of model further in Section 1.4. Interestingly, the latest generation of experiments using modern neutron and synchrotron X-ray sources, together with a number of new theoretical methods, hold promise for bridging the gap between experimental and theoretical studies of structure in disordered materials. For example, new radiation sources have improved the resolution of experimental data, and techniques such as reverse Monte Carlo [3, 4], empirical potential structure refinement [5] and experimentally constrained molecular relaxation [6], are now able to provide a pool of candidate structures consistent with the data. While none of these structures can ever be proven to be 'correct', they can help our understanding of the structure itself, and of the relationships between local structure and other physical properties. See, for example Sheng et al. [7], for a recent application of reverse Monte Carlo to the study of structure in metallic glasses.

In the next section we review some aspects of the phenomenology of supercooled liquids and glasses that will be important for later discussion. In particular, we emphasise the discovery of spatially heterogeneous dynamics which, as we demonstrate in Part I, offers insight into the microscopic relationship between structure and dynamics. More extensive reviews and discussion of other aspects of supercooled liquids and glasses can be found in references [1, 8–15]. Various theoretical models of the glass transition are discussed in other chapters.

1.2 Phenomenology of Supercooled Liquids and Glasses

Far from being unusual, glasses are ubiquitous in the world around us and can be found in many structural and technological applications that exploit both the solid-like and fluid-like nature of glasses, as well as their optical, electrical and magnetic properties. These applications include building materials, household utensils, objects of art, photoconductors, optical fibres, computer memory elements, the rewritable CD and solar cells. Rawson [8] and Zallen [9] provide many more examples. Metallic glasses have greatly increased the range of possible applications due to their exceptional mechanical strength, magnetism in ferromagnetic alloys, atomic smoothness, and ability to be easily molded into complex shapes. Their properties and applications are discussed in more detail in Chapter 4. Many insects, micro-organisms and seeds also protect themselves against harsh environmental conditions by loading their cells with a glass-forming liquid or encasing themselves in a glassy coat of sugars. Research is also being carried out to investigate the glassy properties of carbohydrates for the preservation of food and protein-derived drugs [17, 18]. In addition to metal alloys, glass-formers include oxide glasses (e.g. SiO_2), polymeric glasses (e.g. polystyrene), simple molecular organic glasses (e.g. glycerol), hydrogen-bonded fluids (e.g. water)

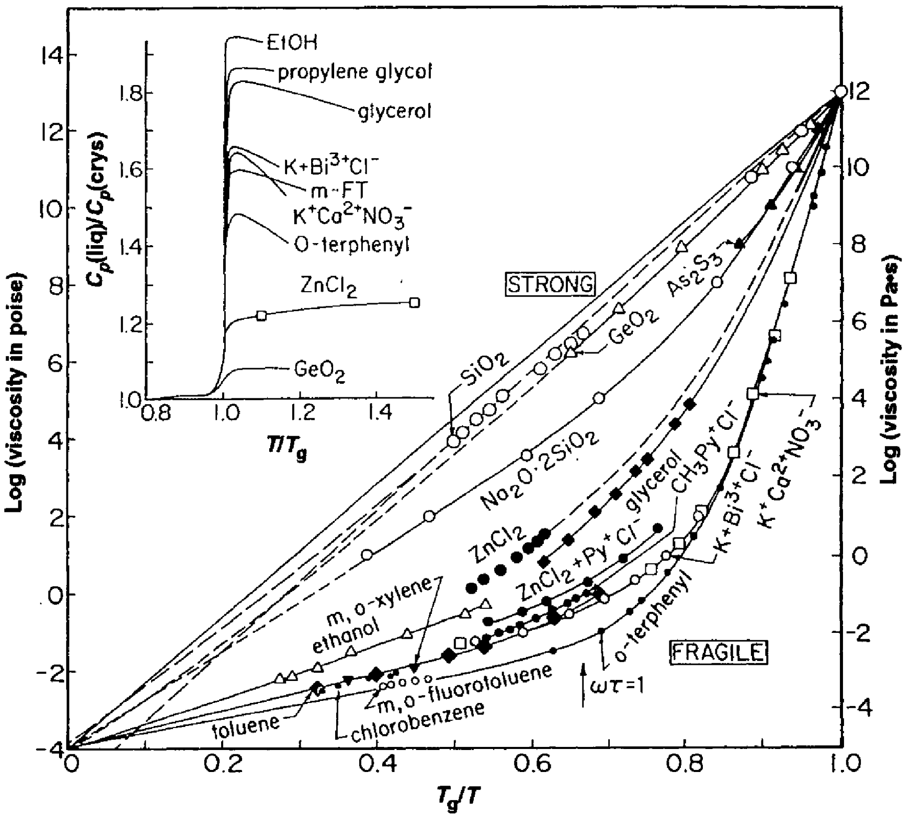

Figure 1.1: Arrhenius plots of viscosities scaled by T_g, the temperature at which the viscosity $\eta = 10^{13}$ P, showing strong and fragile extremes of supercooled liquid behaviour. The inset shows that, in general, strong liquids have small heat capacity jumps at T_g, whereas fragile liquids have larger steps. Hydrogen bonding enhances the drop in the heat capacity at T_g. Reproduced from Angell [16].

and ionic glasses (e.g. $ZnCl_2$). Of these, alloys are among the structurally simplest. Despite their variety, glass-formers all share much common phenomenology.

All glass-formers reach the solid state via a continuous transition from the liquid, with an accompanying large increase in their viscosity η, sometimes over a relatively narrow temperature range. In Figure 1.1 the increase in viscosity as the glass transition temperature T_g is approached has been compared for a variety of different glass-formers. Here T_g is defined as the temperature at which the viscosity reaches 10^{13} Poise. For some glass-formers, for example covalent network glasses, the increase follows an Arrhenius law as indicated by the straight line. These are generally referred to as strong liquids. However, for many glass-formers, the increase in viscosity near T_g shows a strongly non-Arrhenius behaviour as indicated by the non-linear increase in viscosity. These are commonly referred to as fragile liquids. The deviation from

Arrhenius behaviour is often quantified by a ‘fragility’ parameter, that is large for fragile glass-formers and small for strong glass-formers.

The transition into the glassy state is accompanied by a rapid change in thermodynamic derivatives such as the isobaric heat capacity $C_p = (\delta H/\delta T)_P$, where H is the enthalpy. This change occurs over a small temperature interval, resulting in a well-defined step in C_p on cooling at constant pressure, as shown in the inset to Figure 1.1. These rounded discontinuities are the most apparent and commonly used signatures of the glass transition in the laboratory. The drop in C_p - to within a few percent of the heat capacity of the crystal - on cooling through the glass transition is due to the loss of some configurational degrees of freedom on the experimental timescale. Simple molecular and ionic liquids, which have short range structures that are quite sensitive to temperature changes, exhibit large C_p jumps at the glass transition. In contrast, network glass-formers, which form tetrahedrally coordinated three-dimensional networks that undergo very little structural change around T_g, have very small C_p changes. These differences are also visible in the inset of Figure 1.1.

One consequence of this dynamic transition is that the density of the final amorphous state depends upon the quench rate. Figure 1.2 shows the specific volume (volume per unit mass) V as a function of temperature T for a typical liquid. Upon cooling from a high temperature, the liquid may crystallize at the melting/freezing temperature T_m. This is a first order transition which results in an abrupt discontinuity in V. A liquid that manages to pass T_m without crystallising, typically by cooling at a faster rate, is called a supercooled liquid. Although this is strictly a metastable state, supercooled liquids may be stable for years and in the absence of crystal nuclei can be regarded as equilibrium states since their thermodynamic properties are reproducible and independent of thermal history.

As the supercooled liquid is cooled to lower temperatures, its viscosity and density rapidly increase, and the molecules that comprise it slow down. Eventually, the time required for relaxation to the equilibrium configuration becomes comparable to or exceeds the experimental timescale, i.e. the inverse of the cooling rate. At this stage, the liquid falls out of metastable equilibrium and, at a temperature not much lower than this, behaves like a rigid solid (the glassy state). This change from fluid-like to solid-like properties occurs continuously over a temperature interval called the *glass transition* region. The glass transition temperature T_g lies somewhere in this region and can be defined operationally in a number of ways, one common definition being

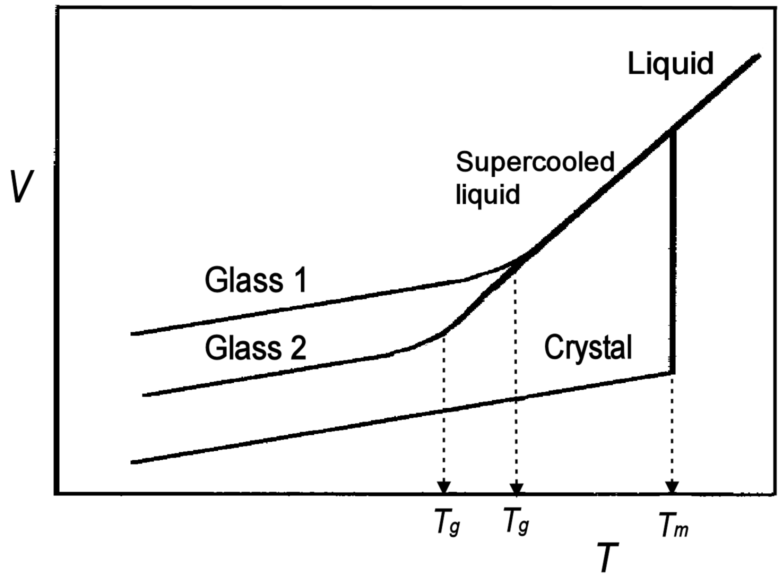

Figure 1.2: A schematic representation of the specific volume V as a function of temperature T on cooling for a typical glass-forming liquid. If the quench rate is sufficiently high, the liquid can be supercooled below the freezing point into a glassy state which depends on the cooling rate. Glass 1 is prepared at a faster cooling rate than Glass 2. The glass-transition temperature T_g decreases as the cooling rate decreases.

the temperature at which the average relaxation time reaches 10^2 s. Both T_g and the width of the transition region depend on the cooling rate. Smaller cooling rates allow the liquid to stay in metastable equilibrium until lower temperatures, and higher quench rates cause the transition region to widen. This is particularly prominent in computer simulations of glasses where the cooling rate is typically greater than 10^{10} K s^{-1}. The glass transition, at least as observed in the laboratory, is not a thermodynamic phase transition, but rather a kinetic event.

Besides the thermodynamic signatures of the glass transition and the rapidly increasing relaxation times as T_g is approached, there are dramatic changes in the *manner* in which supercooled glass-forming liquids relax towards equilibrium following a perturbation such as a change in temperature, pressure or applied external field. In the following discussion we consider only small perturbations such that the response of the system is independent of the sign and magnitude of the perturbation, i.e. linear relaxation.

The return of an observable, such as the dielectric modulus, to its average value following a perturbation can be monitored by a relaxation function X. At temperatures above and just below T_m, X often displays simple exponential behaviour ($X = exp[-t/\tau]$), characteristic of processes dominated by a single activation energy. However, as T_g is approached many supercooled liquids exhibit departures from this simple exponential decay. Such non-exponential relaxation can be reasonably well described by a stretched exponential function of the form $X = Aexp[-(t/\tau)^{\gamma}]$, where $0 < \gamma < 1$, indicating a distribution of relaxation times in the system. There is a rough correlation between the value of the exponent γ and the degree of departure from Arrhenius temperature dependence of relaxation times, i.e. the degree of fragility. Strong liquids typically have γ values close to 1, while fragile liquids tend to have exponents in the range 0.3–0.5. An extensive compilation of γ values and degrees of fragility for about 70 glass-forming systems is provided by Böhmer et al. [19].

The above discussion has focused on the main relaxation process which gives rise to viscous flow in supercooled liquids. This is generally referred to in the literature as the primary or α relaxation. A number of faster relaxation processes have also been identified. The only one that we will refer to in the present work is the *fast* β process. A variety of experiments - neutron scattering [20–22], depolarised light scattering [23–25] and nuclear magnetic resonance [26] - as well as molecular dynamics simulations [27, 28], have now clearly shown that for several diverse glass-forming liquids there exists a fast relaxation process on the *picosecond* timescale. In contrast to the α process, the fast β relaxation has an Arrhenius temperature dependence. Figure 1.3 shows the decay of the incoherent scattering function for *ortho*-terphenyl as measured by neutron scattering. The relaxation curves broaden with decreasing temperature until first a shoulder and then a plateau appears at intermediate times. Both the width and height of the plateau increase with decreasing temperature. The initial decay to the plateau is associated with the fast β process and the second decay from the plateau is associated with the α process.

Measurements of incoherent scattering functions by dynamic light scattering [29, 30], inelastic neutron scattering [31] and neutron spin-echo [32] experiments are often carried out at wavevectors at, or close to, the main peak of the static structure factor. This is because the most intense peak in the structure factor k_{max} provides a measure of the lengthscale for the dominant short-range ordering in the system. The decay of density correlation functions, such as the incoherent scattering function, at wavevectors k close to k_{max} therefore provides information on the main structural

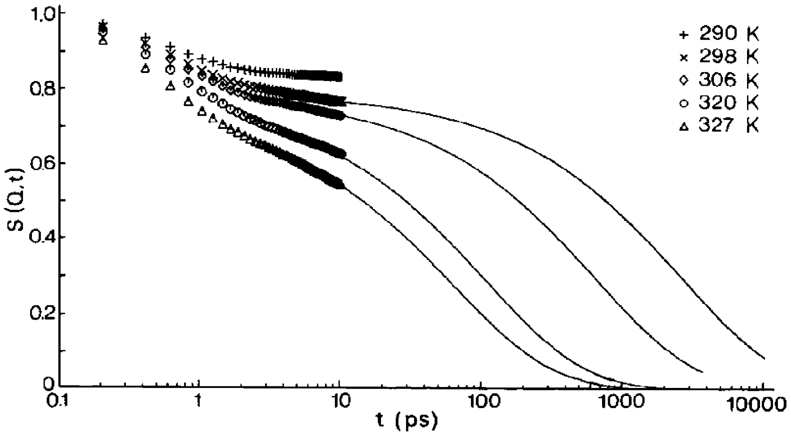

Figure 1.3: Temperature dependence of the intermediate scattering function for *ortho*-terphenyl as observed by incoherent neutron scattering. Note the appearance of a two-step relaxation function with the first decay occuring on the picosecond timescale. Figure reproduced from Kiebel et al. [22].

relaxation process in the system.

Crystallisation is a serious problem for a supercooled liquid on its way to the glassy state. In order to avoid crystallisation, the cooling rate must exceed the maximum rate of crystal nucleation and growth, R_c. This rate has a maximum because below T_m there are two competing effects. Initially, the increasing thermodynamic driving force towards crystal nucleation, due to the growing free energy difference between the supercooled liquid and the crystal, causes the rate to increase. At lower temperatures, however, the increase in viscosity causes diffusional processes to slow down and the rate to decrease. Below T_g, the rate of structural relaxation is so small that crystal nucleation and growth are not a problem. It is therefore only in the intermediate temperature region below and near T_m that the risk of crystallisation is high. Theories of the rates of crystal nucleation and growth and their implications for glass-formation are provided by Turnbull et al. [33–35] and Uhlmann [36]. These studies show that if T_g lies closer to T_m, then the maximum in R_c also moves towards T_m with a decrease in both the height and width of this peak. Thus, crystallisation can be avoided with a lower cooling rate. This change is due to the narrower temperature interval over which the viscosity increases, and the fact that the viscosity near T_m is often greater if T_g is close to T_m. Good glass-formers like *ortho*-terphenyl and SiO_2, which require only slow cooling rates (< 0.1 K s^{-1}) to be quenched into the glassy state, generally have a ratio of $T_g/T_m \approx 0.7$; the latter also has a high viscosity on the order of 10^6 P at T_m [37,38]. In addition, mixtures usually have a greater glass-forming ability than the individual pure components because of the depression in T_m. For example, metal alloys are easier to quench into the glassy state than elemental metals. For alloys, the glass-forming ability is greatest near the eutectic composition where the gap between T_m and T_g is smallest.

An intriguing aspect of the glass transition is that the slowing down, and associated increase in the complexity of the dynamic behaviour, occurs without an obvious structural cause. X-ray and neutron scattering studies of supercooled liquids generally show only subtle changes in local packing associated with a viscosity change of 12 orders of magnitude [39, 40]. In the next section we introduce a recent discovery that may help to address this question.

1.2.1 Spatially Heterogeneous Dynamics

Liquids do not become glasses homogeneously. Tammann [41] suggested as much as far back as 1933, and with the accumulation of data from experiments and simulations of dynamic heterogeneities in supercooled liquids [11,14,42,43], we can now state the situation more explicitly. The transition to rigidity involves the appearance of slowly relaxing domains whose dimensions and lifetimes increase with supercooling. In this section we briefly review some of the evidence from simulations and experiments for the existence of spatially heterogeneous dynamics.

An example of spatially heterogeneous dynamics in a supercooled soft-disc liquid is shown in Figure 1.4. The particle displacement vectors have been plotted over a timescale that is an order of magnitude *longer* than the timescale for α-relaxation. For the 2D mixture that these displacements are taken from, this corresponds to a time five orders of magnitude longer than the average time between particle collisions. The particle displacements are shown as arrows connecting the initial and final positions of each particle. It is clear that some of the particles have moved long distances, while there are large domains of particles that have hardly moved at all. If this was a normal liquid the displacements over this timescale would be similar for all the particles.

Simulations of many different model systems have found direct evidence for such spatially heterogeneous dynamics on intermediate timescales. Foley and Harrowell [45] studied the two-dimensional facilitated kinetic Ising model and found that the relaxation rates were spatially correlated, i.e. that slow spins tend to form 'islands'

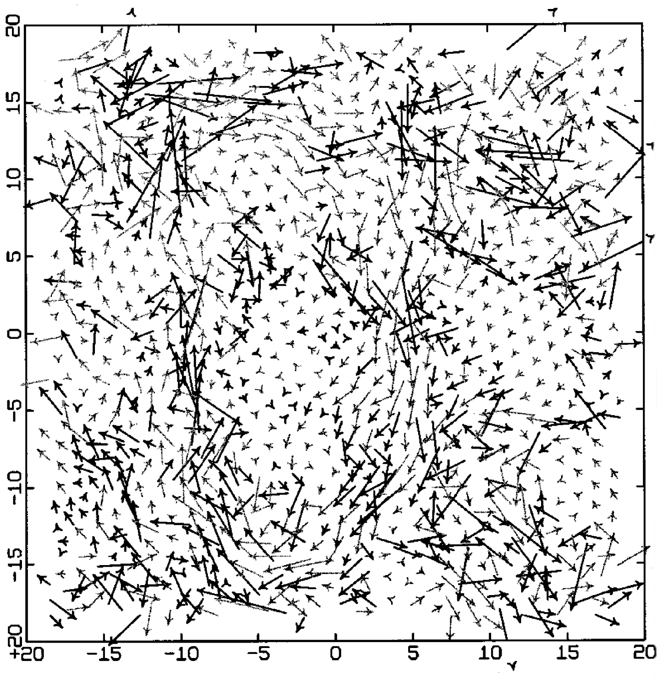

Figure 1.4: The particle displacements, indicated as vectors joining the initial to final particle positions, for particles in a binary soft-disc mixture over a timescale that is an order of magnitude longer than that characteristic of the main α-relaxation. Reproduced from Perera and Harrowell [44].

on the background formed by fast spins; and Kob et al. [46] found that 'mobile' particles in a supercooled 3D Lennard-Jones liquid tend to form clusters whose sizes grow with decreasing temperature. The purely repulsive 2D model, for which the particle displacements are plotted in Figure 1.4, has also been found to have spatially heterogeneous dynamics [44], and similar dynamics has been observed in a number of other 2D [47, 48] and 3D [49, 50] models. Perera and Harrowell [51] have also shown that the assumption of dynamic heterogeneity in a diffusing defect model naturally leads to many of the dynamic properties associated with supercooled liquids, including strong and fragile behavior, two-step relaxation processes, nonlinear relaxation following temperature jumps, spatially correlated kinetics, and non-Gaussian behavior of incoherent processes.

While experiments on supercooled liquids cannot, in general, directly access such structural information, there are now a wide range of experiments that support the existence of heterogeneous dynamics in fragile glass-formers. These include such diverse techniques as NMR [52], solvation dynamics [53], and optical [54] and dielectric dynamic hole burning [55]. A number of other experimental results have been attributed to the existence of *spatially* heterogeneous dynamics. These include the breakdown of scaling between translational and rotational diffusion at low temperature [56], the appearance of non-Fickian or dispersive transport [57], and the dependence of T_g on film thickness in free-standing polymer films [58].

The first experimental technique to actually measure a dynamic correlation length - and thus provide strong experimental evidence for spatially heterogeneous dynamics as opposed to purely heterogeneous dynamics - was a 4D NMR spin diffusion technique introduced by Tracht et al. [59] in 1998. It uses a specially developed technique to selectively magnetise domains of slow particles. This magnetisation then spreads quickly from particle to particle via proton spin diffusion on a timescale that is fast with respect to the particle motion until eventually the magnetisation is spread evenly among slow and fast domains. By selectively measuring how long it takes for the magnetisation in the slow domains to decay and knowing how fast the magnetisation travels, it is possible to calculate a lengthscale for the slow domains. Lengthscales for a range of materials including glycerol, ortho-terphenyl and poly(vinyl acetate) have been measured using this technique. Typical lengthscales obtained are of the order of 1.0–3.7 nm [60].

With these and many other experiments and simulations carried out over the past ten years, there is now indisputable evidence that spatially heterogenous dynamics is a general feature of fragile supercooled liquids. In a sense, this inhomogenous slowing down answers the question of how the transition from liquid to solid can be continuous, and provides an explanation for many of the unusual dynamic properties of supercooled liquids. However, this phenomenological account of the glass transition neatly sidesteps an important question, namely what is responsible for the slow domains? It is an intriguing notion that it could be due to some property of the structure. While experiments are only able to detect subtle changes in the average structure on cooling, the large spatial variation in dynamics appears to contain much information about what aspects of structure are important for dynamics. This is discussed further in Part I.

In the next section we contrast the picture of dynamics in supercooled liquids with that of normal liquids and crystalline solids. We emphasise the transition from mean-field to fluctuation-dominated behaviour during glass-formation and the challenges this poses for any complete theoretical description of glass-formation.

1.3 On the Applicability of Mean-Field Theories near the Glass Transition

Self diffusion in a simple liquid above its melting point is generally well described by mean-field theory, whether one looks at the problem via kinetic theory or a generalised Langevin with memory [61] (the latter including the mode coupling treatments of the memory function [62]). These theories are mean-field in the sense that the dynamics are determined by the average structure of the liquid. In contrast, diffusion in solids is dominated by rare fluctuations in the structure - point defects, dislocations and grain boundaries. As happens whenever kinetics are subject to rare events (nucleation phenomena or fracture, for example), the associated theory treats the relevant fluctuations explicitly rather than trust to the dubious accuracy of the wings of distributions. This is certainly the case in the extensive theoretical literature concerning the defect and grain-boundary mediated transport in solids [63].

The continuous transition from fluid to solid associated with the glass transition traverses between these two extremes. This imposes serious challenges for any complete theoretical description of the glass transition. Can a single theory describe a range of behaviour that at one extreme is well predicted by averages and at the other extreme depends upon rare events? The conceptual transition from mean-field to fluctuation-dominated is perhaps not immediately evident from the literature. The major theoretical treatment of the glass transition - the mode coupling theory (MCT) [62] - incorporates the average liquid structure through vertex functions. This qualifies the MCT as a mean-field theory. The term ‘mean-field’, however, does require some qualification. A hierarchy of generalised Langevin theories can be imagined in which the neglect of fluctuations (the ‘mean-field’ approximation) occurs at increasingly higher orders of correlations. Szamel [64] has recently presented a mode coupling theory of relaxation in a simple lattice model of a glass in which the factorisation is applied to one order higher in correlation to that of the standard approximation. This theory captures scaling laws previously thought to be obtainable only from an explicit treatment of the rare fluctuations responsible for dynamics [65].

In spite of its mean-field character, the evidence that the mode coupling theory can provide a quantitative treatment of diffusion and structural relaxation leading up to the glass transition is impressive [62]. The more recent success of mode coupling theory in providing a unified treatment of colloidal glasses and associating gels is quite remarkable [66]. The problem is that the transition itself - the ideal glass transition - is an artifact of the mathematical structure of the self-consistency introduced by the factorisation approximation. From one point of view, this is an attractive feature of the model - the fact that arrest enters naturally without having to burden the treatment with all the physical correlations that actually stabilise the solid. On the question of the actual physical origins of rigidity of the glass, however, the mode coupling theory is silent. It is necessary to look elsewhere to understand the relationship between structure and dynamics in the liquid as this rigid state is approached.

1.4 This Work

We study the relationship between structure and dynamics in 2D glass-forming alloys by approaching the problem from two directions: (i) by directly examining the spatial distribution of structure and structure-determined dynamics in a binary soft-disc mixture; and (ii), by varying one of the interaction parameters in the model and studying what effect this has on the structure, dynamics and phase behaviour of the system. In Part I we take the former approach, developing new techniques to explore the structural origin of the spatially heterogeneous dynamics that has been widely observed in supercooled liquids. In particular, we consider a binary soft-disc mixture whose glass-forming ability has previously been studied in detail [44, 67]. Then, in Part II, we explore the parameter space of the binary soft-disc model. We study the effect of varying both the interparticle potential and the composition, and show that this simple model is able to form a wide variety of phases, including substitutionally ordered crystals, a range of structurally different glasses, and several phase separated systems. Each has interesting properties (some of which we explore further) and some comparisons are made between the different systems. Finally, in Chapter 8, we discuss how further insight may come from comparing the relationship between structure and dynamics in the initial model with the glass-formers discovered in Part II.

We choose to study the binary soft-disc model for several reasons. The purely repulsive potentials make it one of the simplest models in which real particle dynamics can be studied, and the 2D nature of the model allows for direct visual analysis and comparison of the spatial distribution of both structural and dynamic properties. As already mentioned, the system that we study in Part I - which also forms the starting point of the exploration of parameter space in Part II - has previously been studied in detail and found to reproduce the full range of phenomenology of glass-formation. While there are some differences between the structure and dynamics of 2D and 3D systems, we note that there are also very large variations among different 3D glass-formers. Ultimately, there is insight to be gained from a complete description of any glass-former. If this is not achievable in relatively simple 2D systems then one must ask what hope is there for understanding more complex glass-formers. We therefore expect that the physical insight gained from studying binary soft-disc mixtures will be useful for improving our understanding of real 3D alloys and glass-formers.