Part II

Structural Phases in Non-Additive Soft-Disc Mixtures: Glasses, Substitutional Order, Random Tilings and Segregation
Chapter 4

Introduction and Overview of Results

Ultimately, all the structural, dynamic and thermodynamic properties of glass-formers must be determined by the interaction potentials acting between their constituent atoms or molecules. Therefore, one way to study the relationship between these properties is to systematically vary the interaction potentials and see what effect this has on the system. With this as motivation, we explore the parameter space of the binary soft-disc model. The goals of this work are: (i) to discover what other types of order and phase behaviour this model is able to reproduce; (ii) to gain some insight into the stability of the glass-forming system investigated in Part I; and (iii) to discover if there are related systems that can form amorphous solids, and to compare and contrast their structural and dynamic properties and thus gain further insight into the relationship between structure and glassy behaviour.

The binary soft-disc model that we explore in this part forms two-dimensional analogues of many of the structures observed in real alloys. To put our study into context, we therefore provide a brief introduction to the use of particulate models in structural studies and to the range of structures formed by alloys, with particular emphasis on amorphous alloys. We then provide an overview of our exploration of the parameter space of the binary soft-disc model (presented in detail in the following three chapters), including a discussion of the philosophical approach behind this work and a summary of the main results.
4.1 The Use of Particulate Models in Structural Studies

The use of simple models in the study of liquids and glasses has a long history. Bernal [146] introduced the idea of analysing random packings of spheres. Spheres were placed in bags, shaken and allowed to settle in various ways, before glue was poured over them. The geometry of the sphere-sphere contacts were then analysed in agonising detail. Such early geometric analysis gave birth to the concept of geometric frustration. The densest local packing of uniform spheres in 3D is the tetrahedron, however regular tetrahedra cannot pack together to fill space completely [147]. There is therefore competition between the densest local packing and the need to fill space resulting in frustration. Models of the glass transition have been based on this concept (see ref. [148] for a recent review).

Thermal effects were initially approximated crudely by shaking. In some cases elaborate mechanical devices were built to mix different sized spheres randomly and to shake planar arrays of such mixtures [149,150]. More recently, molecular dynamics simulations have allowed for the correct treatment of the equations of motion, and the use of more realistic models, including long-range potentials and the ability to study non-spherical molecules, e.g. water. However, the study of disc- and sphere-like ‘atoms’ has remained an important way to gain physical insight into the structure and dynamics of real systems. For example, such simple models can reproduce much of the phenomenology of real glass-formers and remain important tests for our understanding of the physics behind glass-formation. One of the most widely studied 3D glass-formers, introduced by Kob and Andersen [151], consists of a binary mixture of particles with spherically-symmetric Lennard-Jones interactions. Simple models also remain important for understanding the structural details of other processes, e.g. crystal nucleation and growth [152], and the competition between crystallisation and glass-formation [153]. Their continued relevance is perhaps because many properties of real materials, including alloys, appear to be dominated by packing effects.

4.1.1 Studies of 2D Models

Because of their relative simplicity, two-dimensional (2D) models have been important for addressing a wide range of problems in condensed matter physics. The most commonly studied models involve particles interacting via hard-disc (hard interactions),
4.1 The Use of Particulate Models in Structural Studies

soft-disc (purely repulsive interactions) and Lennard-Jones (LJ) potentials. The LJ potential has both repulsive and attractive parts and is therefore the most similar of these to real atomic potentials. While these potentials are all isotropic, i.e. independent of direction, anisotropic potentials have also been investigated. Historically, single-component systems were studied first. However, binary and polydisperse mixtures tend to be more interesting because of their added structural and dynamic complexity. For example, binary mixtures are generally more suited to the study of glass-formation because the amorphous state is kinetically stabilised by the additional compositional fluctuations necessary for crystallisation to occur. Problems that have been addressed include the formation, structure and stability of crystals [154–158], quasicrystals [159–161] and glasses. In particular, glass-formation has been studied in binary hard disc mixtures [162], polydisperse hard disc mixtures [48], binary LJ mixtures [163–166], and binary soft-disc mixtures [44,67,167]. Recently, a 2D model consisting of LJ particles with an adjustable anisotropy has been shown to span the full range of glass behaviour from fragile to strong [168]. 2D models have also been used to study ordering in monolayers of charged colloids [169] and dipolar hard spheres [170], of interest for creating nanostructured devices through self-assembly. In the remainder of this section we briefly summarise some research on soft-disc systems, since the thesis constitutes a major extension of these studies. Additional discussion of relevant work can be found in Chapters 5–7.

The one component soft-disc model was studied by Broughton, Gilmer and Weeks [85,171], who used molecular dynamics (MD) to characterise the melting and freezing transitions, and to calculate equations of state for the crystal and liquid phases along with the thermodynamic freezing temperature. And the additive binary mixture that we studied in Part I, has been studied before in the context of glass-formation by Muranaka and Hiwatari [167], and by Perera and Harrowell [44,67]. Bocquet et al. [172] studied the effect of starting with a one-component system and gradually increasing the diameter of half the atoms while simultaneously reducing the diameter of the other half, keeping constant the mean diameter and the temperature. They found a discontinuous transition to an amorphous solid at a critical size ratio of the two species equal to 0.78. In comparison, non-additive soft-disc models have received almost no attention. Mountain and Harvey [173] used MD and Monte Carlo simulations to study a non-additive mixture with $\sigma_{12} > \sigma_{11} = \sigma_{22}$, in which they observed first-order fluid-fluid phase separation. We are not aware of any previous
studies of ordered crystals, crystallisation or glass-formation in non-additive soft-disc mixtures, nor of any studies of ordered crystals or crystallisation in additive soft-disc mixtures.

Despite their simplicity, these models form many of the different types of order observed in real alloys, including substitutionally ordered crystals, quasicrystals and amorphous solids. We therefore provide a brief introduction to alloys and the range of structures that they form in the next section.

4.2 Alloys and Alloy Structures

Alloys are solutions or compounds of two or more elements, at least one of which is a metal. They have metallic properties and are usually designed to have properties which are more desirable than those of their components. For example, steel is harder than its principal component iron. In addition to forming a wide variety of periodic crystalline structures [174, 175], alloys also form more complex structures, including quasicrystals and glasses. Alloys can also micro-segregate when cooled from the melt, resulting in a composite of several different phases.

Periodic crystalline structures have long-range translational order that can be succinctly described by a relatively simple unit cell and rules for translating it to fill space. In substitutionally ordered crystals, the unit cell consists of two or more elements each with distinct environments, while in substitutionally disordered crystals the unit cell consists of a single solvent element with the other solute element(s) randomly substituting for it thus forming a solid solution. Structural defects are well-defined in crystalline alloys and many material properties are now well understood in terms of these [2]. The study of crystal nucleation and growth is an active area of research that we discuss further in Chapter 6.

Quasicrystals (QCs) belong to the family of aperiodic crystals. They produce sharp diffraction peaks just like periodic crystals, but lack long-range translational order. Quasicrystals are remarkable in that some of them display five-fold symmetry. Prior to their discovery in 1982 [176], it was thought that five-fold crystal symmetry could never occur, because there are no space-filling periodic tilings, or space groups, which have five-fold symmetry. They also have some potentially useful properties including low wettability in contact with most aqueous solutions, low coefficients of friction, and low thermal conductivity. Hence there is great interest in resolving the
details of their physical structure. While the physical structure of quasicrystals is still an area of debate (which we discuss further in Section 5.1), a quasiperiodic pattern of points can be formed from a periodic pattern in some higher dimension. For example, to create the pattern for a one-dimensional (1D) quasicrystal, you can start with a regular grid of points in two-dimensional (2D) space. Let the 1D space be a linear subspace that passes through 2D space at an angle. Take every point in the 2D space that is within a certain distance of the 1D subspace. Project those points into the subspace. If the angle is an irrational number such as the golden mean, the pattern will be quasiperiodic. This geometric approach is a useful way to analyze physical quasicrystals. In a crystal, flaws are locations where the pattern is interrupted. In a quasicrystal, flaws are locations where the 1D ‘subspace’ is bent, or wrinkled, or broken as it passes through the higher-dimensional space. In 2D, a quasiperiodic structure can also be formed by a suitable tiling of squares and equilateral triangles. The relationship between quasicrystalline order, random tilings and amorphous solids is discussed further in Chapter 5.

Alloys can form another type of aperiodic crystal known as an incommensurately modulated structure (IMS). While modulated structures are not discussed further in this thesis, we describe them here for the sake of completeness. They can be considered as resulting from a 1D, 2D or 3D displacive and/or substitutional modulation of an underlying periodic structure. When the periods of the modulation wave and the basic structure are incommensurate to each other, an aperiodic crystal is formed, referred to as an IMS. The modulation wavevector may continuously vary with temperature or pressure running through all rational and irrational multiples of the lattice parameters. At low temperatures IMSs often undergo a transition to a periodic phase (the irrational wavevector locks in at a rational value), which can be described as a commensurately modulated phase.

Amorphous alloys, like other glasses, lack any form of long-range order. While the details of their structure is an unsolved problem, recent progress has been made which we review in the next section. Not only are they among the structurally simplest glasses, but they also have a number of useful properties - e.g. high strength, corrosion resistance and soft magnetism - the exploitation of which depends upon better understanding of their structure and phase behaviour. Questions of interest include how to make them more stable to crystallisation, and how to add small domains of crystalline order to improve their toughness. Many alloys, including the first
one made in 1959 [177], require very high cooling rates to avoid crystallisation and can therefore only be formed in very thin strips. Recently, however, new alloys have been discovered that form glasses at much lower cooling rates [178, 179]. As these cooling rates can be achieved by simple casting into metallic molds it has become possible to make a much greater diversity of shapes. Perhaps the most useful property of bulk amorphous alloys is that they are true glasses, which means that they soften and flow upon heating. This allows for easy processing, such as by injection molding, in much the same way as polymers. As a result, amorphous alloys have been commercialised for use in sports equipment, medical devices, and as cases for electronic equipment [180]. However, metallic glasses at room temperature are not ductile and tend to fail suddenly when loaded in tension. Therefore, there is considerable interest in producing composite materials consisting of a metallic glass matrix containing particles or fibers of a ductile crystalline metal.

The structure that a particular alloy, or model, will adopt when cooled is determined by both thermodynamics (stability) and kinetics (speed of formation). Depending on their thermal history, many alloys will micro-segregate into a composite material consisting of two different phases. The interfaces between the two phases can be very elaborate [181], for example, steel can microsegregate into the crystalline phases ferrite and cementite in a layered (lamellar) pattern to form pearlite. In addition to segregation into different crystal phases, alloys may microsegregate in other ways, amorphous-quasicrystal (nanoquasicrystalline) and amorphous-crystal (nanocrystalline) materials being two recent discoveries [182, 183]. Such composite materials are often desirable because they combine good properties of both components, e.g. the hardness of metallic glasses with the toughness of ductile crystalline alloys. Consequently, the study of transitions between these different types of order is of interest for both practical [183, 184] and fundamental [185] reasons.

### 4.2.1 The Structure of Amorphous Alloys

The lack of long-range order in amorphous alloys led early researchers to compare their structure to Bernal’s ‘dense random packing of hard spheres in liquids’ [186]. In this model, the larger solvent atoms are packed densely but randomly and the solute atoms fill the resulting cavities. Gaskell later proposed a stereochemically-defined model, in which the local packing consists of atom clusters in fixed ratios [187] with the same structure as that of crystalline compounds with similar composition. We now
know that the attractive interactions between atoms of different types in amorphous alloys, and their differences in size, result in short-range order (SRO) that can be described by clusters of ‘solute’ atoms of one type surrounded by atoms of a more numerous species referred to as the solvent. However, amorphous alloys also possess medium-range order (MRO), typically over 3–5 atomic diameters. How the clusters of atoms interconnect to generate this MRO is only just starting to become clear, as we describe below.

Miracle [188] recently proposed a model in which face-centred cubic (fcc) packing of overlapping clusters is the building scheme for amorphous alloy structures. This model has been able to predict the compositions of most glass-forming alloys, and of alloys - known as eutectics - with lower melting points than any of their constituents [189], but has not been structurally verified. Sheng et al. have since used a combination of experimental and computational techniques to resolve the atomic level structure of a number of binary nickel-based and zirconium-based amorphous alloys with different ratios of atomic sizes and different solute concentrations [7]. They found that the SRO consisted of a large range of different solute-centred coordination polyhedra, but that these tend to be dominated by certain classes depending on the effective atomic size ratio ($R$) between the solute and solvent atoms. In order of decreasing $R$ these were: the Frank-Kasper type; the icosahedral type; the bi-capped square archimedean antiprism; and the tri-capped trigonal prism. They also found that the MRO was dominated by three types of structures in order of increasing solute concentration: the icosahedral packing of solute-centred quasi-equivalent clusters; the dense packing of ‘extended’ clusters (pairs and strings); and a network-like arrangement of solute atoms. Additionally, they found that the fcc packing previously proposed gave a poorer fit to the experimental data for some transition metal-metalloid alloys. Fernandez and Harrowell have identified similar extended clusters in a well-known model of a metal-metalloid glass former (the Kob-Andersen model) [190]. They found that the extended clusters were composed of local coordination polyhedra with shared triangular faces, and propose that it is the stability of these triangular-faced polyhedra that suppress crystallisation of the preferred CsCl crystal phase.

Thus, a clearer structural picture is gradually forming of both the SRO and MRO in amorphous alloys. This will likely be important for further applications involving these materials, which are already used commercially because of their special magnetic and mechanical properties. In particular, it appears that better understanding of
the relationship between their structural and dynamic properties will be important. For example, more extensive use of their mechanical properties depends on better understanding of their plastic deformation [191]. And the path to understanding their stability to crystallisation in terms of their structure is already being forged [153, 190, 192–194]. The additional stability to crystallisation of the bulk metallic glasses is likely due to the addition of solute species of appropriate sizes and concentrations to fit into the holes left behind by the packing of solute clusters. Therefore a detailed understanding of the atomic packing geometry is likely to be important for the design of new bulk metallic glasses.

The work presented in this part of the thesis identifies, among other phases, a new set of structurally different but related model glass-formers. While we do not expect these to be good structural models for any real metallic glass-formers, we do expect they will help us to gain further insight into the physical principles behind the structure and dynamics of amorphous alloys and the relationship between the two. As stated previously, 2D models are especially attractive because, compared to 3D systems, it is relatively simple to directly visualise both the structure and the dynamics.

4.3 Overview of Model and Results

4.3.1 The Binary Soft-Disc Model

In this part of the thesis we explore the parameter space of the binary soft-disc model. This simple model consists of particles interacting via purely repulsive potentials of the form

$$u_{ab}(r) = \epsilon \left( \frac{\sigma_{ab}}{r} \right)^{12}$$

(4.1)

where the subscripts $a$ and $b$ specify particle types (either 1 or 2 for the binary model). Scaling the dimensions by $\sigma_{11}$, it is clear that there are only two independent length scales, $\sigma_{12}$ and $\sigma_{22}$. The entire parameter space for the model is therefore a 3D space in $\sigma_{22}$, $\sigma_{12}$ and $x_1$, the fraction of particles of type 1. For this study we fixed $\sigma_{22} = 1.4$, the value for the model glass-former studied in Part I, and investigated the effect of varying $\sigma_{12}$ from 1.0–1.3. We considered both equimolar mixtures ($x_1 = 0.5$) and non-equimolar mixtures with $x_1 \approx 0.317$, and characterised the structure, dynamics and phase behaviour of the different systems. Figure 4.1 illustrates the
region of the parameter space that was explored.

It is interesting to study the variation of $\sigma_{12}$ for several reasons. Firstly, while both the one-component and binary soft-disc models have been studied extensively, the effect of making the interparticle potential non-additive has received far less attention, as was discussed in Section 4.1.1. Secondly, by changing $\sigma_{12}$ from additive (i.e. equal to $[\sigma_{11} + \sigma_{22}] / 2$) to non-additive, it should be possible to tune the model from a system in which there is no chemical ordering to a system in which there is strong chemical ordering. Although this is a purely repulsive system, by decreasing $\sigma_{12}$ it is possible to create an effective attraction between unlike species, since the $PV$ term in the Gibbs free energy is able to be reduced when there are more contacts between unlike particle species. Similarly, by increasing $\sigma_{12}$ it is possible to create an effective repulsion between like particle species. This is interesting because glassy alloys appear to fall into two main groups: (i) the random alloy glasses (RAGs) - generally metal-metal, in which chemical ordering is insignificant; and (ii) the chemically ordered glasses (COGs) - generally metal-metalloid, in which there is strong chemical ordering. The additive soft-disc system studied in Part I falls into the former group, while the Kob-Andersen model falls into the latter. The binary soft-disc model may therefore allow

Figure 4.1: Parameter space of the two-component soft-disc model. The dashed line indicates the set of additive parameters, and divides the space into two regions: (a), in which there is an effective attraction between unlike particle species; and (b), in which there is an effective repulsion between unlike particle species. The solid line at $\sigma_{22} = 1.4$ indicates the part of the parameter space explored by the present work.
us to compare the relationship between structure and dynamics in several related, but structurally different, glass-formers.

In total, six systems were investigated. Detailed studies of these are presented in the following three chapters. First, however, we provide an overview of the phase behaviour of the different systems to illustrate some of the interesting comparisons that can be made between them. These comparisons are the ultimate goal of the work presented in this part of the thesis.

4.3.2 Low-temperature Phases

As our results demonstrate, this simple three-parameter model is able to form a wide variety of structurally distinct solid phases, including substitutionally ordered crystals, amorphous solids, random tiling-like structures and multiphase systems. Here we present an overview of the different types of low-temperature structures that were found. Representative configurations are shown in Figures 4.2. The equimolar mixtures with \( \sigma_{12} = 1.0 \) and 1.1 freeze to form substitutionally ordered crystals. Configurations corresponding to their ideal solid-state structures are shown in (b) and (d), which we will refer to as the S1 and H2 structures, respectively. They are related by a slight distortion and merging of adjacent square S1 unit cells. We investigate the process of freezing for the H2 crystal and discuss its stability to supercooling in Chapter 6. In contrast, when the non-equimolar mixtures with the same interparticle potentials are cooled they form solids lacking long-range periodic order, shown in (a) and (c). We argue that these are good glass-formers. For comparison, a configuration of the additive glass-former studied in Part I, i.e. the equimolar mixture with \( \sigma_{12} = 1.2 \), is shown in (f). The non-equimolar mixture with the same additive interparticle potential forms the structure shown in (e) when it is cooled gradually, i.e. it forms a partially phase separated multiphase system consisting of crystalline and amorphous regions, and offers the intriguing possibility of studying the coexistence between crystalline and amorphous states. Cooling of the equimolar mixture with the effectively repulsive interparticle potential \( \sigma_{12} = 1.3 \) results in liquid-liquid phase separation and freezing into two single-component crystalline phases, as shown in Figure 4.3.
4.3 Overview of Model and Results

Figure 4.2: Low-temperature phases obtained upon cooling the following systems: (a) $\sigma_{12} = 1.0$, $x_1 = 0.3167$; (b) $\sigma_{12} = 1.0$, $x_1 = 0.5$; (c) $\sigma_{12} = 1.1$, $x_1 = 0.3167$; (d) $\sigma_{12} = 1.1$, $x_1 = 0.5$; (e) $\sigma_{12} = 1.2$, $x_1 = 0.3164$; and (f) $\sigma_{12} = 1.2$, $x_1 = 0.5$. The small and large particles are represented by filled and open circles respectively.
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Figure 4.3: Low-temperature phase obtained upon cooling the system with \( \sigma_{12} = 1.3, x_1 = 0.5 \). The small and large particles are represented by filled and open circles respectively.

4.3.3 Comparison of Amorphous States as the Interparticle Potential is Varied

Representative low-temperature configurations for the two non-additive glass-formers identified by the present work, and for the additive glass-former studied in Part I, are shown in Figure 4.2, plots (a), (c), and (f). These form a complete structural range of alloy glasses from random alloy to chemically ordered. As the degree of chemical ordering increases, i.e. as \( \sigma_{12} \) decreases from additive, the number of dominant local environments decreases, the structure becomes more homogeneous, and the medium-range order becomes more defined. The structures also differ with respect to the amount of crystalline order that they incorporate. The random alloy - plot (f) - has substantial regions of large particle crystallites, while the glass-former with \( \sigma_{12} = 1.1 \) - plot (c) - shows very little sign of these or of the H2 crystal environment. And the glass-former with \( \sigma_{12} = 1.0 \) - plot (c) - is noteworthy because it appears to have very well-defined local order and obvious structural defects. Its structure can be described in terms of a decorated random tiling of squares and equilateral triangles with additional defects. The structural and dynamics properties of these new glass-formers are characterised in detail in Chapters 5 and 6.

As was discussed in Part I, the presence of structural variations in the random alloy glass-former has a significant impact on its dynamic properties. Therefore, given the structural differences just described, it should be insightful to use the tools
developed in Part I to compare the effect of structure on dynamics over this range of glass-forming systems. In Chapter 8 we provide a taste of where this may lead.

### 4.3.4 Phase Diagrams for the Binary Soft-Disc Model

In Figure 4.4 we compare the different phases formed as a function of the interparticle potential $\sigma_{12}$ and the composition $x_1$. The drawn lines are visual guides and do not necessarily correspond to actual phase boundaries. They do however suggest that the phase space is roughly divided into three regions: (i) a substitutionally ordered crystal region in the top left; (ii) a glass-forming region extending diagonally across the parameter space; and (iii) a phase separated region at the right. Intriguingly, the glass-former studied in Part I, i.e. the equimolar mixture with $\sigma_{12} = 1.2$, is balanced between the extremes of phase separation on the one hand, and formation of a substitutionally ordered crystal on the other [compare Figure 4.2(f) with Figures 4.3 and 4.2(d)].

![Figure 4.4: Different phases formed by the various soft-disc mixtures investigated in this work. Filled squares indicate substitutionally ordered crystals, open squares indicate glass-forming systems, the split hexagon indicates crystal-amorphous coexistence, and the split square indicates liquid-liquid phase separation resulting in coexistence between the single-component large- and small-particle crystal phases $X_L$ and $X_S$, respectively. The lines are speculative phase boundaries and may not be correct.](image-url)
Figure 4.5: Phase diagrams for the binary soft-disc model with $\sigma_{22} = 1.4$ and (a) $x_1 = 0.5$ (b) $x_1 = 0.317$. The black squares represent the approximate melting point of different substitutionally ordered crystals (the error bars indicate the extent of the melting/freezing hysteresis region in our studies). The half-filled squares represent the freezing point of the large particle crystalline phase $X_L$, and the half-filled hexagons represent the freezing point of the small particle crystalline phase $X_S$. The open squares indicate when the supercooled liquid falls out of equilibrium, roughly the temperature at which $F_{s,1}(k, 10^3 \tau) = 0.2$, where $F_{s,1}(k, t)$ is the incoherent scattering function for the small particles calculated at the wave vector corresponding to the largest peak in the respective structure factor $S_{11}(k)$. The lines roughly indicate proposed phase boundaries, and the regions in which we expect glass-formation to be possible.

We used our results to construct tentative phase diagrams for the binary soft-disc model as a function of $\sigma_{12}$. Figure 4.5(a) summarises the phase behaviour of the equimolar mixture, and Figure 4.5(b) summarises the phase behaviour of the $x_1 = 0.317$ mixture. Since the substitutionally ordered S1 and H2 crystals are related by a continuous deformation of the unit cell, we have indicated these by a single ‘binary crystal’ region. ‘Tilings’ refers to a large number of different structures that can be described as decorated tilings of squares and equilateral triangles. We expect the ground state for the non-equimolar mixture in the vicinity of $\sigma_{12} = 1.1$ to be coexistence between the binary crystal and the large particle crystalline phase $X_L$. For the equimolar additive mixture, we have used data from ref. [67] for the freezing points of the large and small particle crystalline phases. Given the small number of data points, the lines defining the stability of the different phases are highly speculative, especially as $T \to 0$. They do, however, provide a sense of the change in phase behaviour of the binary soft-disc model as the interparticle potential is varied, and of the relationship between the different phases.
Chapter 5

The S1 Crystal and a Defected Random Tiling ($\sigma_{12} = 1.0$)

The binary soft-disc mixture with $\sigma_{12} = 1.0$ forms low-temperature structures that can be interpreted in terms of tilings of squares and equilateral triangles. Such tilings have previously been used as models for glass-formers and quasicrystals. We study the structure and dynamics of both equimolar and non-equimolar ($x_1 = 0.3167$) mixtures in the fluid-solid phase region. We find that the equimolar mixture readily freezes into a crystalline solid that we will refer to as the S1 crystal. Both cooling and heating traverses are characterised. In contrast, the non-equimolar mixture forms an amorphous solid state when cooled, yet a crystalline structure with almost identical composition is found to undergo a first order melting transition when heated. This leads us to speculate on the relationship between random tilings, quasicrystals and amorphous structures.

5.1 Square-Triangle Tilings and Quasicrystals

The set of model parameters studied in this chapter allows four large particles to pack almost perfectly around one small particle (the ideal $\sigma_{12}$ length with all else fixed would be $\sqrt{2 \times (1.4)^2/2} \approx 0.9899$). Ideal particle packings for this system can therefore be described as decorated tilings of squares - decorated with 4 large and 1 small particle - and equilateral triangles - decorated with 3 large particles (see Figure 5.1(a)). These two structural units can further pack together to give a total of four different types of large-particle vertices, also shown in Figure 5.1, whose relative
abundance depends on the composition and particular arrangement of particles. Most compositions have the potential to form several different structures with unique vertex frequencies. This model may therefore be suitable for studying the physical effects of solid state entropy. Both regular tilings - with translational and rotational order - and random tilings - with only rotational order - can be constructed.

Square-triangle tilings have previously been used as structural models for real materials. Kawamura [195] studied the statistical mechanics of random square-triangle tilings in the context of amorphous systems, while Frank-Kasper phases [196] can be described in terms of ordered layers of particular square-triangle tilings. Random square triangle-tilings have also been used as a model for twelvefold-symmetric quasicrystals [197], and the structure of some alloys with twelvefold quasicrystalline order have been described in terms of dodecagonal tilings by equilateral triangles and squares [198, 199]. Intriguingly, a recent review [185] of phase transitions in metal alloys found that many alloys have amorphous to quasicrystal phase transitions upon de-vitrification suggesting that these two types of order may be strongly related.

We limit the current investigation to two compositions. An equimolar mixture that readily freezes into a 2D version of the CsCl lattice, which we will refer to as the S1 structure (after a similar packing constructed by Likos and Henley [155]), and a non-equimolar mixture whose composition $x_1 = 0.3167$ was specifically chosen to maximise the configurational entropy of the solid state. Nienhuis [200] has explicitly
calculated the entropy of square-triangle tilings and shown that the configurational entropy is sharply peaked when the area occupied by triangles is equal to the area occupied by squares. It is straightforward to show that this corresponds to a number ratio of squares to triangles of $\sqrt{3}/4$, which with the particle decoration shown in Figure 5.1(a) corresponds to a small particle fraction of $x_1 = 0.31699$ (to 5 d.p.). It is an interesting question how the high configurational entropy of the solid state at this composition affects the nature of the fluid-solid phase transition.

Several particulate models that form square-triangle tilings are already known. Weber and Stillinger [158] studied the melting and freezing of a 2D binary mixture of Lennard-Jones (LJ) particles with 2- and 3-body interactions that crystallises into the same S1 structure as our equimolar mixture, and the structure of a dense randomly packed one-component 2D liquid has been interpreted in terms of tilings of squares and triangles [201]. Leung, Henley and Chester have made extensive use of another LJ model, with the same composition as our non-equimolar mixture, to investigate the stability of quasicrystals (see, for example, ref. [159]). The ratio of squares to triangles at which the maximal configurational entropy occurs also happens to be the ratio at which a subset of the tilings have quasicrystalline order.

Simulations of 2D binary LJ models have observed spontaneous formation of random-tiling like structures that lack ideal quasiperiodic order but which have long-range 10- or 12-fold orientational order and which produce quasicrystal-like diffraction patterns (with peaks that may be sharp or broad depending on the model) [159, 160]. Widom et al. [160] have argued that one of these models is stabilised by the high configurational entropy of the random tilings, and in a later paper [161] demonstrated that its thermodynamic ground state was indeed crystalline.

In contrast, a recent review [202] of experimental work on quasicrystals provides strong evidence that: (i) at least one real quasicrystal has near-ideal quasiperiodic order (not just on average); (ii) that this structure can be well-described by a packing of overlapping symmetry-breaking decagons proposed by Grummelt [203]; and (iii) that this structure is energetically, not entropically, stabilised. They do, however, concede that the structure of some quasicrystals may be well described by a random packing of clusters which on average produce high symmetry. The precise structural and energetic relationship between 2D and 3D quasicrystals remains to be fully understood.

The rest of this chapter is structured as follows. The model and computational
methods are described in Section 5.2, and in Section 5.3 we characterise the structural and dynamic properties of the equimolar mixture for both heating and cooling traverses. Our study of the non-equimolar mixture is presented in Section 5.4. We characterise the structural and dynamic changes during cooling from the liquid state to an amorphous solid, and in Section 5.4.4 we show that a periodic solid with similar composition undergoes a discontinuous melting transition. This is followed by a summary of the main results and a comparison of the structure and phase behaviour of the two mixtures in Section 5.5.

5.2 Model and Computational Details

We consider a 2D system consisting of a binary mixture of particles interacting via purely repulsive potentials of the form

\[ u_{ab}(r) = \epsilon \left( \frac{\sigma_{ab}}{r} \right)^{12} \]  

(5.1)

where \( \sigma_{12} = 1.0 \times \sigma_{11} \) and \( \sigma_{22} = 1.4 \times \sigma_{11} \). All units quoted will be reduced so that \( \sigma_{11} = \epsilon = m = 1.0 \) where \( m \) is the mass of both types of particle. Specifically, the reduced unit of time \( \tau = \sigma_{11} \sqrt{m/\epsilon} \). A total of \( N \) particles were enclosed in a square box with periodic boundary conditions - except for one set of runs (described in Section 5.4.4) for which the particles were enclosed in a rectangular box with periodic boundary conditions.

The molecular dynamics simulations were carried out at constant number of particles, pressure \( (P = 13.5) \) and temperature using the Nosé-Poincaré-Andersen (NPA) algorithm developed by Laird et al. [83, 84]. This algorithm is discussed further in Appendix A, where we also list the equations of motion in 2D. The equations of motion were integrated using a generalised leapfrog algorithm [84]. The time step employed was 0.05\( \tau \) for \( T > 1 \), and 0.01\( \tau \) for \( T \leq 1 \). For argon units of \( \epsilon = 120k_B \), \( m = 6.6 \times 10^{-23}g \) and \( \sigma_{11} = 3.4\,\AA \), these time steps correspond to approximately 10 and 20 femtoseconds respectively.

A non-equimolar mixture consisting of \( N_1 = 456 \) small particles and \( N_2 = 984 \) large particles (giving \( N = 1440 \) and \( x_1 = 0.3167 \) to 4 d.p.) was studied at 31 different reduced temperatures from \( T = 5 \) to \( T = 0.2 \). The starting configuration of the run at \( T = 5 \) was an equilibrated configuration at \( T = 5 \) for the equimolar system described in Chapter 6 with the appropriate number of small particles changed to
5.3 Freezing and Melting of the Equimolar Mixture

large particles. The starting configuration of each lower temperature equilibration run came from the final configuration of the preceding higher temperature run. For $T \geq 0.5$, the equilibration times were longer than the times taken for all the dynamic correlation functions investigated to decay to zero. Below $T = 0.5$ the system is no longer able to reach equilibrium within the finite timescale of the simulations. Thus, the computer glass transition temperature for these simulations, defined as the temperature at which the system falls out of equilibrium, lies between $T = 0.5$ and $T = 0.45$. At all temperatures, the equilibration runs were taken out until steady state was achieved, i.e. until the average thermodynamic properties remained constant in time. Table C.6 (in Appendix C.2) lists the temperatures of each state studied as well as the equilibration and production times. The final configurations of the equilibration runs were used to start the production runs. The ‘masses’ of the Anderson piston and Nosé thermostat were $Q_v = 0.002$ and $Q_s = 1000$, respectively, for all temperatures.

Both cooling and heating traverses were studied for the equimolar mixture. Tables C.1 and C.2 (in Appendix C.1) list the temperatures of each state studied as well as the equilibration and production times for the cooling and heating traverses, respectively. The initial configuration for the cooling traverse was an equilibrated configuration at $T = 5$ for the equimolar system described in Chapter 6 with a total of $N = 1440$ particles, while the initial configuration for the heating traverse was the constructed periodic structure shown in Figure 5.4(a) that has a total of $N = 1444$ particles. The starting configurations for production runs and for lower (or higher) temperature equilibration runs are as described above for the non-equimolar mixture. The ‘mass’ of the Nosé thermostat was $Q_s = 1000$ for all temperatures. For the cooling traverse, the ‘mass’ of the Anderson piston was $Q_v = 0.0002$ for $T \geq 1.1$ and $Q_v = 10^{-6}$ for $T \leq 1.08$. For the heating traverse, $Q_v = 10^{-8}$ for all temperatures.

5.3 Freezing and Melting of the Equimolar Mixture ($x_1 = 0.5$)

5.3.1 Thermodynamic Properties

The thermodynamic averages for the potential energy per particle ($U$), energy per particle ($E$), enthalpy per particle ($H$), and number density per particle ($\rho$) are
summarised in Table C.1 for the cooling traverse, and in Table C.2 for the heating traverse, for the range of temperatures that were investigated. Also tabulated are the compressibility factor ($Z = P/(\rho T)$), the coupling constant $\Gamma = \rho T^{-1/6}$, as well as the root mean square (rms) deviations of the instantaneous thermodynamic properties from their averages, calculated as $\sqrt{\langle x^2 \rangle - \langle x \rangle^2}$ where $x$ is the property of interest and the angular brackets indicate an average over time.

The isobaric phase diagram for the equimolar mixture is shown in Figure 5.2. For the cooling traverse there is a clear step increase in density at $T = 1.02$, suggesting a first order freezing transition between $T = 1.02$ and $T = 1.04$. The resulting solid continues to have slightly lower density than the constructed perfect S1 crystal, which is consistent with the presence of defects that are frozen-in (see Figure 5.3 for representative configurations). When the constructed crystal is heated, there is a clear step decrease in density at $T = 1.08$, indicative of a first order melting transition between $T = 1.06$ and $T = 1.08$. The resulting liquid has the same density as the liquid for the cooling traverse. The different positions of the steps in density for the cooling and heating traverses indicate a region of hysteresis extending from $T = 1.02$–1.08 over which the liquid and solid phases are metastable to supercooling and superheating, respectively. The thermodynamic freezing temperature $T_f$ should lie somewhere in this region.
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5.3.2 Structural Properties

Particle Configurations

Representative particle configurations from the cooling traverse are shown in Figure 5.3. Several changes in structure can be identified. At $T = 2$ the particles are well mixed and there is little recognisable order. Neither of the particle species form large clusters. By $T = 1.04$, i.e. just before freezing, there are large clusters of crystalline domains, characterised by squares of four large particles surrounding one small particle packed together. After the step increase in density at $T = 1.02$ (see Figure 5.2) there is obvious long-range order in the system, consistent with this being a

![Figure 5.3: Representative particle configurations for the cooling traverse at (a) $T = 2$, (b) $T = 1.04$, (c) $T = 1.02$, and (d) $T = 0.7$. The small and large particles are represented by filled and open circles respectively.](image-url)
freezing transition. The units of S1 squares packed together are easy to identify. There are some defects in the crystal - mainly of the interstitial/vacancy and substitutional types - which appear to decrease in number with further cooling.

Representative particle configurations from the heating traverse are shown in Figure 5.4. The regular order of the equilibrated crystal at $T = 0.4$ has become somewhat less regular by $T = 1.06$, and a few defects are visible, but the long-range periodic order remains. At $T = 1.08$ there is still significant clustering of S1 units but the long-range order has been lost. This is where the step decrease in density occurs (see Figure 5.2, and is consistent with this being a melting transition. By $T = 1.02$ there is less crystalline order in the liquid.

Figure 5.4: Representative particle configurations for the heating traverse at (a) $T = 0.4$, (b) $T = 1.06$, (c) $T = 1.08$, and (d) $T = 1.2$. The small and large particles are represented by filled and open circles respectively.
5.3 Freezing and Melting of the Equimolar Mixture

Pair Distribution Functions

The pair distribution functions describe the radially averaged structure about particles. They are a useful way to identify long-range translational order and also contain much information about the local structure in a system. For an isotropic substance, the pair distribution function (PDF) is defined as

\[
g_{\text{all}}(r) = \left\langle \frac{1}{N\rho} \sum_i^N \sum_{j \neq i}^N \delta[r - r_{ij}] \right\rangle,
\]  
(5.2)

where \(N\) is the total number of particles, \(\rho\) the number density, \(r_{ij}\) the separation between two particles, and the angular brackets denote an average over different configurations in time.

For two component systems, there are three partial pair distribution functions (PPDFs):

\[
g_{ab}(r) = \frac{1}{x_ax_bN\rho} \left\langle \sum_i^{N_a} \sum_j^{N_b} \delta[r - r_{ij}] \right\rangle, \quad a, b = 1, 2,
\]  
(5.3)

where \(\rho\) is the total number density, \(x_a = N_a/N\) is the number fraction of species \(a\) with \(N = N_1 + N_2\), and the prime in the second summation indicates that terms for which \(i = j\) are omitted when \(a = b\).

The PDF and PPDFs for the cooling traverse are plotted in Figures 5.5 and 5.6. They all show a clear transition from medium to long-range translational order between \(T = 1.04\) and \(T = 1.02\), which confirms a transition from liquid to crystalline order at \(T = 1.02\) during the cooling traverse. There are also strong correlations prior to freezing, with solid-like structure in the PDFs extending out to at least \(8\sigma_{11}\). Note, however, that there is significant change in \(g_{11}(r)\) local structure both before and during freezing. The first peak shifts from \(r = 1\) at high temperature to \(r = 1.4\) in the crystalline state, with a change in peak intensity already visible prior to freezing. This can be explained by the disappearance of small particle nearest neighbours (with an expected separation distance of \(r = 1\)), to a local structure where small particles are contained in square cells of the type shown in Figure 5.1(a). When these are packed together the expected small-small separation is equal to \(\sigma_{22} = 1.4\). To distinguish this change in local order, we use the first minimum in \(g_{11}(r)\) at \(T = 1.04\) as the cutoff for defining small particle nearest neighbours below \(T = 1.04\). The definition of nearest neighbours is discussed further below. A consequence of this shift in peak
intensity - and the associated weak local ordering - is that for much of the liquid state the most intense peak in $g_{11}(r)$ is the third one. This is found at $r = 2$ and is likely due to a linear small-large-small particle arrangement. The lack of strong crystalline local ordering of the small particles prior to freezing (as evidenced by the significant change in $g_{11}(r)$) is rather unusual, especially in a 2D system. On the other hand, both $g_{12}(r)$ and $g_{22}(r)$ show strong local crystalline ordering prior to freezing.

The PDF and PPDFs for the heating traverse are plotted in Figures 5.7 and 5.8. These are very similar to those obtained for the cooling traverse at the same temperature, the major difference being that the transition from long-range to short-range translational order occurs between $T = 1.08$ and $T = 1.06$. As for the cooling
traverse, this change in translational order coincides with a discontinuity in the density. Additional structure develops in the PDF and PPDFs at very low temperature, presumably due to a decrease in vibrational motion.

From this data we extract cutoff distances to use for defining nearest neighbours. Two particles of type $a$ and $b$ are defined to be nearest neighbours if they are separated by a distance less than $\text{cut}_{ab}$. This definition of nearest neighbours will be used when calculating various structural properties including the local coordination environment and orientational order parameters. We have generally used the position of the first minimum in $g_{ab}(r)$ as the value for $\text{cut}_{ab}$, as this distance usually allows for the best
distinction between the first and second coordination shells. That said, we have not followed this rule for the current model (with $\sigma_{11} = 1.0$) when defining $cut_{11}$ at low temperature. This is because the first maximum in $g_{11}(r)$ shifts to a substantially larger distance at low temperature that can no longer correspond to a small-small nearest neighbour interaction, as has been explained above. To be able to identify this change in local structure about small particles, we have therefore set $cut_{11}$ at low temperature equal to the smallest value of $cut_{11}$ that was calculated from a minimum following a maximum in $g_{11}(r)$ corresponding to a nearest neighbour interaction.

Cutoff distances for the cooling traverse are listed in Table C.3. For $cut_{11}$ at $T \leq 1.02$ we have used the position of the minimum in $g_{11}(r)$ at $T = 1.04$ for the reasons just explained. Cutoff distances used for the heating traverse were $cut_{11} = 1.32$, $cut_{12} = 1.66$ and $cut_{22} = 1.80$. The latter two values were obtained from the first
minima in the respective PPDFs, while the value for cut$_{11}$ was set equal to the value obtained for the cooling traverse at $T = 1.15$.

**Structure Factors**

The partial structure factors can be calculated from the PPDFs as follows:

$$ S_{ab}(k) = x_a \delta_{ab} + x_a x_b \rho \hat{h}_{ab}(k), \quad a = 1, 2, $$

(5.4)

where $\hat{h}_{ab}$ is the Fourier transform of the total correlation function $h_{ab}(r) = g_{ab}(r) - 1$ and has the form:

$$ \hat{h}_{ab} = \int_0^\infty r h_{ab} J_0(kr) dr $$

(5.5)
for a homogeneous fluid in 2D. $J_0$ is the Bessel function of order 0. We have also calculated the total structure factor

$$S_{\text{all}}(k) = 1 + \hat{\rho} \hat{h}_{\text{all}}(k)$$  \hspace{1cm} (5.6)

where $\hat{h}_{\text{all}}$ is the Fourier transform of $h_{\text{all}}(r) = g_{\text{all}}(r) - 1$. The integrals were evaluated using the extended Simpson’s rule [204].

The structure factors for the cooling traverse, displaced vertically for clarity, are plotted in Figures 5.9 and 5.10. The oscillations at small $k$ for $T \leq 1.02$ are artifacts of the Fourier transformation procedure due to the truncation of the long-ranged pair
distribution functions at non-zero values and should be ignored. As the temperature is lowered, the heights of the peaks become more pronounced, and at $T = 1.02$ they increase dramatically in height and become very sharp.

The location of the most intense peak ($k_{\text{max}}$) represents a characteristic length-scale for the dominant short-range ordering in the system. The decay of density correlation functions at wave vectors close to $k_{\text{max}}$ therefore provides information about the main structural relaxation process in the system. As explained in Section 1.2, measurements of intermediate scattering by dynamic light scattering, inelastic neutron scattering and neutron spin-echo experiments are often made at wave vectors
close to $k_{max}$. We therefore calculate the incoherent intermediate scattering functions (Section 5.15) at the wave vectors corresponding to the first maxima in $S_{11}(k)$ and $S_{22}(k)$. For reference, these are listed in Table C.4. We did not investigate structural relaxation in the solid state and have therefore not calculated structure factors for the heating traverse.

Local Structure Parameters

Several quantities were used to characterise the local structure of the equimolar mixture. In Figure 5.11 we present the ‘bond’ fractions $n_{ab}$ for the cooling and heating traverses. The ‘bond’ fractions are defined as the fraction of all nearest neighbour particle pairs that occur between particles of type $a$ and $b$ (see Section 5.3.2 for the definition of nearest neighbours). They can be related to, and give similar information to, the first shell partial coordination numbers calculated previously for the equimolar mixture with $\sigma_{12} = 1.2$ [67].

The changes in local structure during the cooling and heating traverses are very similar. The majority of nearest neighbour interactions occur between unlike particle species (about 60%), with most of the remaining interactions being between large particles. During cooling, there is a sudden decrease in $n_{11}$ at $T = 1.02$ that is accompanied by smaller step increases in $n_{12}$ and $n_{22}$; and during heating, the reverse occurs at $T = 1.08$. These temperatures coincide with the temperatures at which there are sudden changes in the other properties already studied. In particular, the sudden decrease in small particle nearest neighbours at $T = 1.02$ is consistent with our interpretation that the first peak in $g_{11}(r)$ at this temperature is no longer due to small particle nearest neighbours.

Another way to characterise the change in local structure is via the local coordination environment. We have identified a particular neighbourhood with the following notation: a small particle with $m$ small neighbours and $n$ large neighbours is designated as $S_{mn}$ and the analogous large particle is indicated as $L_{mn}$. The distribution of these local environments is plotted as a function of temperature in Figure 5.12 for both the heating and cooling traverses. Only the most common environments are shown.

As the equimolar mixture is cooled, the fraction of S04 environments - corresponding to the square tile in Figure 5.1 - increases gradually until $T = 1.02$ at which point there is a sudden large increase, followed by a gradual increase as the temperature
Figure 5.11: ‘Bond’ fractions as a function of temperature for the cooling and heating traverses. The filled symbols indicate data from the heating traverse. \( n_{ab} \) is the fraction of all nearest neighbours particle pairs that occur between particles of type \( a \) and \( b \). Error bars represent one standard deviation.

is further reduced. There is a smaller increase in S14 until \( T = 1.02 \) after which the fraction of these environments begins to fall. Both these results are consistent with a freezing transition to the S1 crystal at \( T = 1.02 \); the S14 order could be due to a vibrational distortion of two square S04 environments packed together, which would explain why it decreases when the crystal is cooled. The main changes in large particle environments is a gradual increase in L43 until \( T = 1.02 \) at which point there is a sudden drop followed by a further gradual decrease with cooling. In a perfect S1 crystal the large particles will lie at the centre of four square unit cells packed together - corresponding to vertex (b) in Figure 5.1 - and will thus have an L44 environment. As this quantity was not calculated we can only speculate that the variation in L43 at low temperature is due to this being a vibrational distortion of the L44 environment.

We do know that 52% of local environments are unaccounted for at \( T = 0.7 \). Since the S04 and S14 environments make up about 48% of all local environments at \( T = 0.7 \), and all 5-, 6- and 7-fold environments have been quantified, we assume that most of the remaining 52% is in the form of L44 environments. The other local environments present at high temperature make a negligible contribution below \( T = 1.02 \).

The heating traverse shows very similar variation in the distribution of local environments as a function of temperature. The major difference is that the sudden
Figure 5.12: The distribution of local environments as a function of temperature for (a) heating, and (b) cooling traverses. We have identified a particular neighbourhood with the following notation: A small particle with \( m \) small neighbours and \( n \) large neighbours is designated as \( S_{mn} \) and the analogous large particle is indicated as \( L_{mn} \).
jumps now occur between $T = 1.06$ and $T = 1.08$. All the large particles must be in L44 environments at $T = 0.1$.

**Orientational Order Parameters**

We have already established that the equimolar mixture has long-range translational order at low temperature. Here we define a set of order parameters to investigate the local orientational order and long-range correlations between local environments. Following the definition of a hexatic order parameter by Broughton et al. [171], we define a set family of $n$-fold orientational order parameters for particle $j$ as

$$
\psi_n(r_j) = \frac{1}{n_j} \sum_{k=1}^{n_j} \exp^{i\theta_{jk}}
$$

(5.7)

where $n_j$ is the number of nearest neighbours of particle $j$ at position $r_j$ and $\theta_{jk}$ is the angle (in radians) made by the bond between particle $j$ and particle $k$ and an arbitrary direction (here chosen to be the $x$ axis). The order parameter equals one if particle $j$ lies at the centre of a regular $n$-fold polygon made up of its neighbours.

A set of bulk averaged $n$-fold order parameters can then be defined as follows:

$$
\Psi_n = \left\langle \frac{1}{N} \sum_{j=1}^{N} |\psi_n(r_j)| \right\rangle,
$$

(5.8)

where the partial $n$-fold order parameters are given by

$$
\Psi_{n,a} = \left\langle \frac{1}{Na} \sum_{j=1}^{Na} |\psi_n(r_j)| \right\rangle \text{ with } a = 1, 2.
$$

(5.9)

The angular brackets represent an average over various configurations separated in time.

The bulk averaged $n$-fold order parameters $\Psi_n$ probe the local orientational order. We consider the 4-, 6- and 12-fold order parameters. Both 4- and 6-fold local environments are common in the set of models that we have studied, and a random tiling of squares and triangles (a possible structure for the non-equimolar mixture explored in Section 5.4) will have long-range 12-fold order.

Their temperature variation is plotted in Figure 5.13 for both the heating and cooling traverses. $\Psi_{4,1}$ increases gradually below $T = 1.5$ and undergoes a sudden
Figure 5.13: The temperature dependence of the bulk averaged $n$-fold order parameters $\Psi_n$, where $n = 4, 6, 12$, and their small ($\Psi_{n,1}$) and large ($\Psi_{n,2}$) particle contributions, for the cooling and heating traverses. The filled symbols indicate data from the heating traverse. The error bars represent one standard deviation about the average.
increase at $T = 1.02$ followed by a further gradual increase, very similar to the behaviour of the S04 environment. At the same time there is a decrease in $\Psi_{4,2}$, which can be explained by large particles increasingly finding themselves in vertices of type (b) (see Figure 5.1). The large particles at the centre of these vertices will have L44 environment which, having 8-fold orientational order, will result in $\Psi_{4,2} = 0$. The local 6-fold order decreases suddenly during cooling at $T = 1.02$. The variations in $\Psi_{12,a}$ appears to contain no additional information. The changes in bulk orientational order are similar for the heating traverse, except that the jump in properties now occurs at $T = 1.08$.

Next we test for the presence of long-range orientational correlation between local domains. The spatial correlation of the orientation of the local $n$-fold environments is measured by the associated correlation functions

$$C_n(r) = \left\langle \frac{1}{N\rho} \sum_{j=1}^{N} \sum_{k \neq j}^{N} \psi_n(r_j) \psi_n^*(r_k) \delta(|r_j - r_k|) \right\rangle$$ \hspace{1cm} (5.10)

and

$$C_{n,a}(r) = \left\langle \frac{1}{N\rho x_a^2} \sum_{j=1}^{N_a} \sum_{k \neq j}^{N_a} \psi_n(r_j) \psi_n^*(r_k) \delta(|r_j - r_k|) \right\rangle \quad \text{with} \quad a = 1, 2. \hspace{1cm} (5.11)$$

These orientational correlation functions are weighted by the translational correlations. To see them free of this bias we plot the ratios $G_n(r) = C_n(r)/g_{\text{all}}(r)$, $G_{n,1}(r) = C_{n,1}(r)/g_{11}(r)$, and $G_{n,2}(r) = C_{n,2}(r)/g_{22}(r)$. We consider the cases where $n = 4, 6, 12$ for the reasons outlined above.

In Figure 5.14, we plot the partial 4-fold orientational correlation function $G_{4,1}(r)$ for both the cooling and heating traverses. We have not plotted $G_{4,2}(r)$ as there was no observable structure in this function. The functions have been displaced vertically for clarity. There is clearly long-range 4-fold orientational correlation between small particle environments for $T \leq 1.02$ during the cooling traverse, and $T \leq 1.06$ during the heating traverse, and only local order at higher temperature, which is consistent with the existence of the S1 crystal state at these temperatures. We have also calculated the 6- and 12-fold orientational correlation functions, however as they provide little additional insight we do not plot them. The 6-fold correlation functions have only a single peak and show little variation with temperature, while the 12-fold correlation functions are very similar to the 4-fold correlation functions and can be
explained by the presence of 4-fold order in the system.

In summary, the equimolar mixture freezes at $T = 1.02$ into a largely defect-free S1 crystal structure. There appears to be substantial crystalline order in the liquid prior to freezing, in the form of S04 environments and a large uncounted fraction of local environments most of which are probably L44 environments. There is also evidence for medium-range packing of S04 cells, from the medium-range structure in the pair distribution functions, and from the high proportion of S14 environments. The structural changes during heating from a perfect S1 crystal are very similar, and confirm a region of metastability extending from $T = 1.02$–1.08.
5.3 Freezing and Melting of the Equimolar Mixture

5.3.3 Dynamics and Structural Relaxation

In this section, we present an analysis of the changes in particle transport and structural relaxation that occur upon cooling and heating of the equimolar mixture. We report some of the main time correlation functions that are routinely measured in MD simulations.

Intermediate Scattering Functions

The timescales of structural relaxation can be probed quite readily by computing density correlation functions such as the incoherent and coherent intermediate scattering functions. For the equimolar mixture, we have calculated the incoherent (or

Figure 5.15: The incoherent scattering functions $F_{s,1}(k_1,t)$ and $F_{s,2}(k_2,t)$ for the small and large particles, respectively. The wave vectors $k_1$ and $k_2$ are the first peak positions in the respective partial structure factors (listed in C.4). From left to right the temperatures of the curves are $T = 5, 3, 2, 1.5, 1.2, 1.15, 1.1, 1.08, 1.06,$ and $1.04.$
Figure 5.16: Arrhenius plot of the structural relaxation times $\tau_{\text{e},1}$ and $\tau_{\text{e},2}$ and the inverse diffusion constants $D_{\text{e},1}^{-1}$ and $D_{\text{e},2}^{-1}$ for the cooling traverse. Some inverse diffusion constants calculated for the heating traverse, $D_{\text{h},1}^{-1}$ and $D_{\text{h},2}^{-1}$, are also shown. The dashed lines are linear regressions through the cooling data for $T \geq 1.04$.

The self-intermediate scattering functions

$$F_{s,a}(k, t) = \frac{1}{N_a} \left\langle \sum_{j=1}^{N_a} \exp(ik[\mathbf{r}_j(t) - \mathbf{r}_j(0)]) \right\rangle, \quad a = 1, 2 \quad (5.12)$$

for both particle species. The angular brackets denote an average over time origins and an angular average over the directions of the wave vector $k$. The magnitudes of $k$ were chosen as the positions of the first maxima in the respective partial structure factors. The first peak was used since this is the largest one and therefore the best wave vector at which to monitor structural relaxation. Since the position of this peak varies significantly with temperature, we have used a temperature dependent magnitude for $k$, the values of which are listed in Table C.4.

We have only calculated incoherent scattering functions for the cooling traverse. These are plotted in log-linear form in Figure 5.15 for $T \geq 1.04$, i.e. for the liquid phase. It would be interesting to extend this analysis to the solid phase and to the
heating traverse to further investigate the nature of defect motion in the S1 crystal. We find that the relaxation curves decay smoothly and broaden with decreasing temperature, until at $T = 1.04$ they span over two decades in time. There is no sign of a plateau region at intermediate times.

Structural relaxation times $\tau_{e,1}$ and $\tau_{e,2}$ are defined as the time taken for the incoherent scattering functions $F_{s,1}(k,t)$ and $F_{s,2}(k,t)$, respectively, to decay to $1/e$ of their initial values. The temperature dependences of these relaxation times, plotted in Figure 5.16, appear to be Arrhenius at all $T \geq 1.04$. This is consistent with the equimolar mixture existing as a normal liquid in this temperature range.

### Mean-Squared Particle Displacements

The mean-squared displacement (MSD) can provide important information regarding the dynamics of particles on different length scales, and is defined as

$$R^2(t) = \frac{1}{N} \left\langle \sum_{i=1}^{N} |\mathbf{r}_i(t) - \mathbf{r}_i(0)|^2 \right\rangle,$$  \hspace{1cm} (5.13)

where the angular brackets represent an average over time origins. The MSD is also a useful way to distinguish between a rigid system and a fluid one.

At very short times, the MSD has a power law dependence on time with an exponent of two, which corresponds to ballistic motion. A particle undergoes ballistic motion until it experiences its first collision with another particle, and such motion is therefore present even in systems that are configurationally frozen. The end of this region can therefore be used to estimate the first collision time. At much longer times, if the system is fluid, the MSD has a power law dependence on time with a slope of one, indicating diffusive motion.

A long-time diffusion constant can be extracted from the MSD. For the 2D system this is given by

$$D = \frac{1}{4} \lim_{t \to \infty} \frac{dR^2(t)}{dt}.$$ \hspace{1cm} (5.14)

Strictly speaking, the diffusion constant cannot be defined asymptotically in 2D as, according to the Landau-Peierls theorem [205], it diverges in the thermodynamic limit. However, in practice this is not an issue. The upward curve in the MSD at long times is so slow to appear that the diffusion constant is still well-defined and meaningful on the timescale of the simulations. A comparison of the diffusion
constants and structural relaxation times can sometimes reveal interesting differences in the dynamics of incoherent processes on different length scales.

The MSDs over all particles $R^2(t)$, and averaged over the two particle species, $R_2^2(t)$ and $R_1^2(t)$ are plotted in Figure 5.17 for the cooling traverse and in Figure 5.18 for the heating traverse. All the plots are qualitatively very similar. At very short times, the curves have a power law dependence on time with an exponent of two, which corresponds to ballistic motion, while at much longer times, for sufficiently high temperature, the curves have a smaller slope of one indicating diffusive motion. The first collision time for this system is about $0.01 \tau$. The sudden increase in $R_1^2(t)$ for the heating traverse at $T = 0.9$ is due to the appearance of defect approx. 2000$\tau$ into the production run.

Upon cooling, there is an increasing separation in timescales between ballistic and diffusive motion, accompanied by the sudden appearance of a plateau region at intermediate times at $T = 1.02$. This intermediate region is often associated with transient caging of particles by their neighbours. As we have already described, the structure of the equimolar mixture changes dramatically at $T = 1.02$, consistent with a freezing transition to a defected S1 crystal at this temperature. The MSD curves therefore suggest that there must be significant motion - presumably of the defects - in the S1 crystal. Additional cooling runs would be useful to investigate at what temperature the defect motion eventually stops.

During the heating traverse, only ballistic motion is present at low temperature. The constructed S1 crystal must therefore remain defect free. Eventually, at $T = 0.95$, $R_1^2(t)$ begins to rise again after about 100$\tau$ followed by $R_2^2(t)$ after about 1000$\tau$. For $T \geq 1.08$ the MSD curves again show typical liquid behaviour with no plateau region at intermediate times. A survey of the equilibrated configurations show that the crystal structure remains defect free until $T = 0.95$ at which point a few defects appear. We therefore suggest that it is these defects that are responsible for the rise in the MSD at long times between $T = 0.95$ and $T = 1.06$. We therefore conclude that motion in the defected crystal is dominated by small particles. This contrasts with the behaviour observed after freezing during the cooling traverse when both particle species have similar mobility.

Diffusion constants were measured for both the cooling and heating traverses in the region where the MSD has reached its long-time constant value ($R_a^2(t) > \sigma_{11}^2$). An Arrhenius plot of the inverse diffusion constants is shown in Figure 5.16. They
Figure 5.17: The time dependence of the MSD averaged over all particles $R^2(t)$, and averaged over the two particle species, $R^2_2(t)$ and $R^2_1(t)$ for the cooling traverse. The temperature of the curves from top to bottom is $T = 5, 3, 2, 1.5, 1.2, 1.15, 1.1, 1.08, 1.06, 1.04, 1.02, 1, 0.98, 0.96, 0.94, 0.92, 0.9, 0.8, and 0.7.$
Figure 5.18: The time dependence of the MSD averaged over all particles $R^2(t)$, and averaged over the two particle species, $R_2^2(t)$ and $R_1^2(t)$ for the heating traverse. The temperature of the curves from top to bottom is $T = 1.2, 1.18, 1.16, 1.14, 1.12, 1.1, 1.08, 1.06, 1.04, 1.02, 1, 0.95, 0.9, 0.8, 0.7, 0.6, 0.5, \text{ and } 0.4$. Note that the sudden increase in $R_2^2(t)$ at $T = 0.9$ is due to the appearance of a defect during the production run.
have Arrhenius temperature dependence for the entire liquid region \((T \geq 1.04\) for the cooling traverse, and \(T \geq 1.08\) for the heating traverse). For reference, the structural relaxation times and diffusion constants are also listed in Table C.5. Diffusion constants measured for the defected crystals are generally two orders of magnitude smaller than for the low-temperature liquid.

The Non-Gaussian Parameter

In a harmonic solid, and in an equilibrium liquid at times sufficiently long for particles to randomise the initial distribution of momenta, the probability of a particle displacement of magnitude \(r\) is proportional to a simple Gaussian function \(\exp(-Cr^2)\), where \(C\) is a constant that may depend on time. Substantial deviations from such Gaussian behaviour have been observed in many simulations of supercooled liquids at intermediate times. These deviations can be quantified by a non-Gaussian parameter \([206]\) defined as

\[
A(t) = \frac{R^4(t)}{C[R^2(t)]^2} - 1, 
\]

where \(R^4(t) = \langle |r_i(t) - r_i(0)|^4 \rangle\) is the mean-quartic displacement, \(R^2(t)\) is the mean-squared displacement, and the constant \(C\) equals \(5/3\) in 3D and 2 in 2D. For a Gaussian process \(A(t) = 0\) for all times. Non-Gaussian parameters for individual particles species, represented by \(A_a(t)\), can also be defined by averaging only over particles of type \(a\).

Hurley and Harrowell \([74]\), studying a model of particles undergoing a random walk in a dynamically heterogeneous environment, demonstrated that large values of \(A(t)\) at intermediate times could be attributed to a broad distribution of local mobilities in the system. Thus, the non-Gaussian parameter can be used as a measure of the degree of dynamic heterogeneity. The maximum in \(A(t)\) is expected to increase as the distribution of local relaxation times broadens.

We have calculated the non-Gaussian parameters for both the cooling traverse (plotted in Figure 5.19) and the heating traverse (plotted in Figure 5.20). During cooling, the non-Gaussian parameters remain very small at all times for \(T \geq 1.04\). Suddenly, at \(T = 1.02\), a large peak appears at intermediate times, and upon further cooling the amplitude of the peak and the time at which it occurs increase. During heating, the non-Gaussian parameters remain very small at all times for \(T < 0.9\) and \(T \geq 1.08\). At \(T = 0.9\) a relatively narrow peak of large amplitude appears at relatively late time in \(A_1(t)\) that can be attributed to the appearance of a defect in the crystal.
structure at about 2000$\tau$ into the production run. Between $T = 0.95$ and $T = 1.06$, a large peak again occurs at intermediate times with an amplitude that is larger at lower temperature. The unusually shaped peak at $T = 1.06$ can be attributed to a late onset of large particle defect motion. These results are all consistent with a freezing transition at $T = 1.02$ during cooling and a melting transition at $T = 1.08$ during heating. The appearance of the large peak at intermediate times in the non-Gaussian parameters coincides with the appearance of mobile defects in the crystal structure and can be explained by these. The peaks in $A_2(t)$ during the heating traverse appear at much later times, for the equivalent temperature, than during the cooling traverse. This suggests that the defect motion during the heating traverse is qualitatively different than during the cooling traverse.

Additionally, the large oscillations in $A_1(t)$ are visible between 10$\tau$ and 100$\tau$ during the heating traverse. These coincide with similar oscillations in the plateau region of $R_1^2(t)$ for all $T \leq 1.06$. Similar damped oscillations have been observed in the plateau region of the incoherent scattering functions for several glass-formers including the model studied in Part I. For that particular model, Perera and Harrowell [44] concluded that while system size could influence the frequency of these modes, their presence was a consequence of the transient rigidity of the liquid [44]. The present work demonstrates that such oscillations can also appear in a crystalline solid, either with or without defects. The unusually large size of the oscillations in $A_1(t)$ observed during the heating traverse may be related to the very small ‘mass’ used for the Anderson pressure piston $Q_v$ (see Section 5.2).

Prior to freezing, the structural relaxation times follow an Arrhenius temperature dependence and the equimolar mixture shows typical liquid dynamics. In the solid phase, there is substantial defect motion in the high-temperature crystal, during both the heating and cooling traverses, as evidenced by a late rise in the MSDs and large peaks in the non-Gaussian parameters. During heating defects appear at $T = 0.9$ - initially due to small-particle motion, but at later times also due to large-particle motion. This reduced large-particle mobility contrasts with the frozen crystal in which the small and large particles have almost identical mobilities. The structural and dynamic data for both heating and cooling traverses is consistent with a transition from rigid S1 crystal to crystal with defect motion to normal liquid and vice versa. The equimolar mixture is discussed further in Section 5.5.
Figure 5.19: The non-Gaussian parameter averaged over all particles, $A(t)$, and averaged over only the small and large particles, $A_1(t)$ and $A_2(t)$, respectively, for the cooling traverse. The temperatures of the curves are as listed for Figure 5.17. Observe the sudden change in behaviour at $T = 1.02$. 

5.3 Freezing and Melting of the Equimolar Mixture
Figure 5.20: The non-Gaussian parameter averaged over all particles, $A(t)$, and averaged over only small and large particles, $A_1(t)$ and $A_2(t)$, respectively, for the heating traverse. The temperatures of the curves are as listed for Figure 5.18. Observe the sudden change in behaviour at $T = 1.08$. The sharp peak in $A_1(t)$ at $T = 0.9$ is due to the appearance of a defect during the production run.
5.4 Amorphisation and Melting of the Non-Equimolar Mixture ($x_1 = 0.3167$)

In this section we characterise the thermodynamic, structural and dynamic properties of the non-equimolar mixture. The composition ($x_1 = 0.3167$) was chosen to favour a random tiling with maximal configurational entropy as explained in Section 5.1. A 2D quasicrystal approximant can also be constructed at this composition [159]. When cooled from the fluid state, we find that the mixture forms an amorphous solid with well-defined local order and defects. In contrast, a periodic structure with similar composition melts discontinuously (see Section 5.4.4). This leads us to speculate on the relationship between random tilings, quasicrystal and amorphous solids.

5.4.1 Thermodynamic Properties

For reference, thermodynamic averages for the cooling traverse of the non-equimolar mixture are tabulated in Table C.6. The non-equimolar mixture was studied at many closely spaced temperatures, including at high temperature, to improve confidence in the nature of the transition from liquid to solid. Figure 5.21 shows the isobaric

![Figure 5.21: Isobaric ($P = 13.5$) phase diagram. Error bars represent one standard deviation. Note the lack of a step in density upon cooling.](image-url)
phase diagram for the cooling traverse. The density increases smoothly indicating a continuous transition from the liquid to solid state. There is perhaps a small change in slope at $T = 0.45$, which is when the system falls out of local equilibrium. In the next section we characterise the changes in structure that occur during cooling of the non-equimolar mixture. Only data at selected temperatures ($T = 5, 3, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, 0.3, \text{ and } 0.2$) are plotted.

Figure 5.22: Representative particle configurations at (a) $T = 1$, (b) $T = 0.7$, (c) $T = 0.4$, and (d) $T = 0.2$ for the cooling traverse. The small and large particles are represented by filled and open circles respectively.
5.4 Amorphisation and Melting of the Non-Equimolar Mixture

5.4.2 Development of Random-Tiling Order

Particle Configurations

Selected particle configurations are plotted in Figure 5.22. At high temperature ($T = 1$) the liquid appears homogeneous but there is no clustering of small particles. By $T = 0.7$ local square and equilateral packings are apparent and small regions of S1 crystal order can be observed. These crystalline regions appear to have grown by $T = 0.4$ and the structure is now well described as a random tiling of squares and equilateral triangles with the occasional defect. Most of the structure is now rigid, as can be seen by comparing this configuration with the one after further cooling to $T = 0.2$. However, some changes are apparent in the lower left quarter of the structure indicating that motion is still possible at these very low temperatures.

Pair Distribution Functions

In Figures 5.23 and 5.24 we plot the pair distribution function (PDF) and the partial pair distribution functions (PPDFs), as defined in Section 5.3.2. It is clear that there is no development of long-range translational order on cooling. Some increase in local structure is apparent but this does not extend beyond $r = 7\sigma_{11}$. The most obvious change is that the position of the first peak in $g_{11}(r)$ shifts from $r = \sigma_{11}$ to $r = 1.4\sigma_{11}$ as the temperature is decreased. This is similar to what was observed for the equimolar mixture and can be explained by the disappearance of small particle nearest neighbours. As we demonstrate in Section 5.4.2, the small particles become surrounded by four large particles at low temperature forming the equivalent of square tiles resulting in a small particle closest interaction length of $\sigma_{22} = 1.4\sigma_{11}$. The large intensity of the peak around $r = 2\sigma_{11}$ relative to the first peak in $g_{11}(r)$ is due to a high relative proportion of linear small-large-small particle arrangements and can be explained by the majority of large particle vertices being of types (c) and (d) as illustrated in Figure 5.1. Thus the medium-range order in the non-equimolar mixture is quite different from that in the equimolar mixture. We explore this further in Section 5.4.2.

From these data we extract cutoff distances to use for defining nearest neighbours. We have generally used the position of the first minimum in $g_{ab}(r)$ as the value for $cut_{ab}$. The exception is for $cut_{11}$ where we have used the position of the first minimum in $g_{11}(r)$ at $T = 1.5$ as the cutoff for all $T \leq 1$. This is necessary in order to distinguish
changes in local structure about small particles. Recall that as the temperature
decreases there is a large shift in the position of the first peak to a value no longer
corresponding to a nearest neighbour particle interaction. The following cutoffs were
obtained: \((\text{cut}_{11}, \text{cut}_{12}, \text{cut}_{22}) = (1.44, 1.71, 2.06)\) for \(T \geq 2\), and \((1.37, 1.61, 1.83)\) for
\(T \leq 1\).

The partial structure factors were calculated from the PPDFs as explained in
Section 5.3.2. For reference, they are plotted along with the total structure factor in
Figures C.1 and C.2.
Figure 5.24: The partial pair distribution function \( g_{12}(r) \) and the total pair distribution function \( g_{\text{all}}(r) \) as a function of distance from \( T = 5 \) down to \( T = 0.2 \). For \( T \leq 3 \), each curve has been shifted upwards by one unit from the higher temperature curve directly preceding it.

Local Structure

Several quantities (defined in Section 5.3.2) were used to characterise the local structure of the non-equimolar mixture. The ‘bond’ fractions \( n_{ab} \) are shown in Figure 5.25. The majority of nearest neighbour interactions occur between large particles at all temperatures, closely followed by unlike particle interactions. Upon cooling below \( T = 0.6 \), there is a small step in \( n_{12} \) to lower values and a similar increase in \( n_{22} \), consistent with a small increase in the clustering of large particles. \( n_{11} \) remains very low for all \( T \leq 1 \), indicating that small particles are separated from each other at these temperatures. This is consistent with the earlier observation that the peak in
Figure 5.25: Nearest neighbour ‘bond’ fractions as a function of temperature for $T \leq 1$. $n_{ab}$ is the fraction of all nearest neighbours particle pairs that occur between particles of type $a$ and $b$.

$g_{11}(r)$ around $r = \sigma_{11}$ disappears when the mixture is cooled below $T = 2$ (see Figure 5.23).

In Figure 5.26 the distribution of local environments is plotted as a function of temperature. This analysis reveals that there is more variation in local structure during cooling than was picked up by the ‘bond’ fractions. There is a large gradual increase in the fraction of L25 environments between $T = 1$ and $T = 0.4$ that is accompanied by smaller smooth decreases in the fraction of L34, L24 and L15 environments. There is also a small increase in the fraction of L06 environments. Large particles at the centre of vertices of types (c) and (d) shown in Figure 5.1 will have L25 local order. Thus the increase in L25 order could be due to an increase in the formation of these types of vertices. The presence of some L16 order in the system could be due to slightly distorted L25 environments. The observation that L16 order decreases with temperature is consistent with these being vibrational distortions. The small increase in L06 environments could indicate an increase in the clustering of large particles or an increase in the number of isolated vertices of type (e) in Figure 5.1. Although not calculated, the fraction of L44 environments, corresponding to
5.4 Amorphisation and Melting of the Non-Equimolar Mixture

![Graph showing the distribution of local packing environments as a function of temperature.](image)

**Figure 5.26:** The distribution of local packing environments as a function of temperature. We have identified a particular neighbourhood with the following notation. A small particle with $m$ small neighbours and $n$ large neighbours is designated as $S_{mn}$ and the analogous large particle is indicated as $L_{mn}$.

For small particles, the main changes during cooling are a sudden increase in $S_{04}$ environments at $T = 0.55$ accompanied by a similarly sized decrease in $S_{05}$ order. $S_{04}$ order can be identified with the square tile shown in Figure 5.1(a), while the $S_{05}$ environment is a non-ideal local packing. The substantial fraction of $S_{14}$ order must be due to a vibrational distortion of two $S_{04}$ units packed together, as the peak in $g_{11}(r)$ at $r = \sigma_{11}$ disappears on cooling and we observe no pentagonal $S_{14}$ environments in the low-temperature configurations [see, for example, Figure 5.22(d)]. Reducing the cutoff distance used to define nearest neighbour interactions between small particles would help to better distinguish between $S_{04}$ and $S_{14}$ environments. Below $T = 0.4$ there is little change in any of the local environments, consistent with
Orientational Order Parameters

In order to quantify the orientational order throughout the system we have introduced the \( n \)-fold orientational order parameters (see Section 5.3.2 for their definitions). The temperature variation for the 4-, 6- and 12-fold local order parameters is plotted in Figure 5.27. The major change upon cooling is an increase in the 4-fold order about small particles \( \Psi_{4,1} \) below \( T = 2 \) from 0.4 to 0.7, and a decrease in \( \Psi_{6,1} \) over the same temperature range from 0.45 to 0.25. There is also a small increase in 6-fold order about large particles from \( T = 2–1 \). There are no particles with 12 nearest neighbours so the increase in 12-fold bulk order must be due to the changes in 4- and 6-fold orientational order.

Next we test for long-range orientational correlation of the local domains. In Figure 5.28 we plot the partial 4-fold orientational correlation function about small particles \( G_{4,1}(r) \) and the partial 6-fold orientational correlation function about large particles \( G_{6,2} \). There was no structure in \( G_{4,2}(r) \) and only a small first peak in \( G_{6,1} \), so we do not plot these. Upon cooling, there is a small increase in orientational correlation between 4-fold environments about small particles. The peak structure is complex and different to that observed for the S1 crystal (see Figure 5.14). We therefore conclude that the medium-range order that develops about small particles is not of the S1 crystal type. There is also a similar but smaller increase in structure in \( G_{6,2} \). This peak structure is different from that observed when there are substantial crystalline domains of large particles (see, for example, Figure 7.9), so we conclude that the medium-range order that develops about large particles is not due to crystalline domains of hexagonally-packed large particles, i.e. clustering of type (e) vertices. A random square-triangle tiling would be expected to have long-range 12-fold orientational order, so we plot the 12-fold orientational correlation function in Figure 5.29. There is some growth in the extent of 12-fold orientational correlations between both small and large particle environments, however there is clearly no long-range orientational order in the system. Therefore, we conclude that the local packing defects in this system are sufficient to disrupt this long-range orientational order.

We conclude that the non-equimolar mixture shows no sign of crystallisation or phase separation upon cooling from the liquid state. The low-temperature local structure is dominated by square S04 small particle environments, and L25 large particle
5.4 Amorphisation and Melting of the Non-Equimolar Mixture

Figure 5.27: The temperature dependence of the bulk averaged $n$-fold order parameters $\Psi_n$, where $n = 4, 6, 12$, and their small ($\Psi_{n,1}$) and large ($\Psi_{n,2}$) particle contributions. Error bars represent one standard deviation.
environments. Our results suggest that approximately 50% of large particles find themselves in vertices of type (c) and (d), with another 10-20% each in vertices of type (b) and (e), where the vertex types refer to those in Figure 5.1. Although only 3% of particles find themselves in pentagonal S05 environments, these appear sufficient to disrupt the formation of long-range 12-fold orientational order. In the next section, we present an analysis of the changes in particle transport and structural relaxation that occur during cooling.
5.4.3 Onset of Glassy Dynamics

Intermediate Scattering Functions

The timescales of structural relaxation can be probed quite readily by computing density correlation functions such as the incoherent and coherent intermediate scattering functions. For the non-equimolar mixture, we have calculated the incoherent (or self) intermediate scattering functions $F_{s,1}(k, t)$ and $F_{s,2}(k, t)$ for the small and large particles, respectively (see Section 5.3.3 for their definitions). $F_{s,1}(k, t)$ and $F_{s,2}(k, t)$ have been measured at the positions of the first maxima in the static structure factors $S_{11}(k)$ and $S_{22}(k)$ (plotted in Figure C.1). The positions of these maxima are weakly
Figure 5.30: The incoherent scattering functions $F_{s,1}(k_1, t)$ and $F_{s,2}(k_2, t)$ for the small and large particles, respectively. The wave vectors $k_1$ and $k_2$ are the first peak positions in the respective partial structure factors (listed in Table C.7). From left to right the temperatures of the curves are $T = 5, 3, 2, 1, 0.9, 0.8, 0.7, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, 0.3$ and $0.2$. Note the appearance of a two-step relaxation process at low temperature.

Log-linear plots of the self intermediate scattering functions are shown in Figure 5.30. The relaxation curves broaden with decreasing temperature until below $T = 0.5$ they are no longer able to decay to zero within the finite time scale of the simulations. The relaxation functions already span over five decades in time at these temperatures. At $T = 0.6$ a step appears in the relaxation curves at intermediate times. This step broadens into a plateau with an amplitude that increases with decreasing temperature. The height of the plateau also increases with decreasing temperature. Such two-step relaxation functions have been observed in a wide range of glass-forming systems as discussed in Section 1.2. Damped oscillations are also observed in the
Figure 5.31: Arrhenius plot of the structural relaxation times $\tau_{e,1}$ and $\tau_{e,2}$ and the inverse diffusion constants $D_1^{-1}$ and $D_2^{-1}$. The dashed lines are linear regressions through the data for $T \geq 0.7$. Note the divergence from Arrhenius behaviour at low temperature.

plateau region similar to what has been observed for other glass-formers including the model studied in Part I. Perera and Harrowell [44] concluded that while system size can influence the frequency of these modes, their presence is a consequence of the transient rigidity of the liquid.

Structural relaxation times $\tau_{e,1}$ and $\tau_{e,2}$ are defined as the time taken for the incoherent scattering functions $F_{s,1}(k, t)$ and $F_{s,2}(k, t)$, respectively, to decay to $1/e$ of their initial values. The temperature dependences of these relaxation times, plotted in Figure 5.31, appear to be Arrhenius at high temperature, but diverge strongly from Arrhenius dependence as the temperature drops below $T = 0.7$, behaviour typical of a fragile liquid. Note that the structural relaxation times for the small and large particles are almost identical, which is somewhat unusual.

Mean-Squared Particle Displacements

The mean-squared displacement (MSD) over all particles $R^2(t)$, and averaged over the two particle species, $R_2^2(t)$ and $R_1^2(t)$ are plotted in Figure 5.32. All three plots
Figure 5.32: The time dependence of the MSD averaged over all particles $R^2(t)$, and averaged over the two particle species, $R_{22}^2(t)$ and $R_{12}^2(t)$. The temperature of the curves from left to right is the same as in Figure 5.30.
are qualitatively very similar. At very short times, the curves have a power law dependence on time with an exponent of two, which corresponds to ballistic motion, while at much longer times, for sufficiently high temperatures, the curves have a smaller slope of one indicating diffusive motion. Upon cooling, there is an increasing separation in timescales between ballistic and diffusive motion, accompanied by the appearance of a plateau region at intermediate times. This intermediate region is often associated with transient caging of particles by their neighbours. As for the relaxation curves, the MSDs also show behaviour that is typical of glass-forming systems.

Diffusion constants were measured in the region where the MSD has reached its long-time constant value ($R_a^2(t) > \sigma_{11}^2$). The inverse diffusion constants are plotted against temperature in Figure 5.31. They show a weaker deviation from Arrhenius temperature dependence than the structural relaxation times, with the onset of this deviation occurring around the same temperature, i.e. $T = 0.6$. The ratio $D_1/D_2 \approx 1$ for $T \geq 0.7$ after which it increases slightly with further cooling, i.e. the diffusion constants, like the relaxation times, are almost identical for the small and large particles. For reference, the structural relaxation times and diffusion constants are also listed in Table C.8. In the next section we investigate the appearance of dynamic heterogeneity in the liquid.

Non-Gaussian Parameter

As explained in Section 5.3.3, the non-Gaussian parameters $A_a(t)$ can be used as a measure of the degree of dynamic heterogeneity in a sample. They are plotted for the present system in Figure 5.33. A rapid rise in non-Gaussian behaviour is observed at low temperature for both the large and small particle species. As explained earlier, large values at intermediate times can be attributed to a broad distribution of local mobilities. Therefore, this is evidence that the dynamics in the supercooled liquid is becoming heterogeneous. The maximum value of $A_1(t)$ increases rapidly below $T = 0.7$, while the maxima in $A_2(t)$ show a similar but smaller increase over the same temperature range. The trend is for the maxima to move to longer times as they increase in height; below $T = 0.4$ the finite observation time of the simulations is too short to observe them. $A_2(t)$ and $A_1(t)$ are no longer able to decay to zero below $T = 0.45$. From this, we conclude that the system falls out of equilibrium near this temperature.
Figure 5.33: The non-Gaussian parameter averaged over all particles, $A(t)$, and averaged over small and large particles, $A_1(t)$ and $A_2(t)$, respectively. The temperatures of the curves are as listed in the caption for Figure 5.32. Observe the rapid increase in peak heights with decreasing temperature.
The changes in dynamic properties upon cooling of the non-equimolar mixture - the rapid increase in structural relaxation times, the appearance of a plateau in the incoherent scattering functions and MSDs, the non-Arrhenius temperature dependence of the structural relaxation times and inverse diffusion constants at low temperature, and the onset of non-Gaussian dynamics - are all consistent with what has been observed for other model glass-formers. Our structural analysis found no development of long-range translational or orientational order, or tendency to crystallise or phase separate. Thus the non-equimolar mixture appears to be a good glass-former.

5.4.4 Melting of a Periodic Structure

The continuous transition from fluid to amorphous solid for the non-equimolar system is intriguing. Why does it not freeze into a solid phase with perfect local packing, into either a random or ordered tiling with only square and triangular local order? How does the high configurational entropy of the solid state affect the nature of this phase transition? Is the presence of a few defects sufficient to disrupt a weak first-order transition?

As a first step towards addressing these questions, we constructed and heated a periodic structure with similar composition. The constructed particle packing is shown in Figure 5.34(a), and has vertex frequencies in the ratio $b : c : d : e = 0 : 6 : 6 : 1$, where the vertices are as drawn in Figure 5.1. The book ‘Tilings and Patterns’ [207] contains this and many other examples of periodic square-triangle tilings. In comparison, the ratio of vertex frequencies for a random tiling at this composition is $b : c : d : e = 0 : 1.26 : 11.6 : 1$ [198].

A total of $N = 1444$ particles were enclosed in a rectangular box with periodic boundary conditions in order to accommodate the rectangular unit cell of the crystal. We used a simulation cell with a fixed width:height ratio of $x/y = 0.866$, and the ratio of small to large particles was $N_1 : N_2 = 456 : 988$ giving a composition of $x_1 = 0.3158$. The model parameters and MD algorithm were as described previously in Section 5.2. The NPA Hamiltonian for independent scaling of $x$ and $y$ axes is given in Appendix A.

Only a limited set of equilibration runs were made to probe the nature of the solid to fluid phase transition. The system was equilibrated for $1000\tau$ at reduced temperatures of $T = 0.2$, 0.25, 0.3, 0.35, 0.4, 0.45, 0.5, 0.55, 0.6, 0.65, 0.7, 0.75, 0.8, 0.85 and 0.9. The starting configuration of the run at $T = 0.2$ was the constructed
periodic packing shown in Figure 5.34(a) whereas, for each of the higher temperatures, the initial configuration for the equilibration run came from the final configuration of the preceding lower temperature run. During these runs, the crystalline solid melted at $T = 0.7$. To test for stability to melting, additional 10,000$\tau$ runs were made at $T = 0.65$, 0.6 and 0.55 starting from the final configuration of the initial 1000$\tau$ equilibration runs. The solid melted at both $T = 0.65$ and 0.6 but was stable at $T = 0.55$. We therefore conclude that the melting temperature lies somewhere between $T = 0.55$ and $T = 0.6$. There are some structural defects present at $T = 0.55$ in the form of particle packings that do not correspond to ideal tilings.
5.5 Discussion and Conclusions

Figure 5.35: Isobaric ($P = 13.5$) phase diagram. Note the step in density upon cooling.

Selected configurations before, during, and after melting are shown in Figure 5.34. The latter part of the equilibration runs - when there was no longer any apparent change in thermodynamic properties - was used to obtain values for the equilibrium densities (shown in Figure 5.35). There is a clear step in density between $T = 0.6$ and 0.55. The densities of the liquid state points are very similar to those obtained previously upon cooling.

5.5 Discussion and Conclusions

The equimolar mixture freezes into a largely defect-free S1 crystal structure at $T = 1.02$. There appears to be substantial crystalline order in the liquid prior to freezing, in the form of S04 environments and a large unaccounted for fraction of local environments which are most likely L44 environments. There is also evidence for medium-range packing of S04 cells. The structural changes during heating from a perfect S1 crystal are very similar, and confirm a region of metastability extending from $T = 1.02$–1.08. Prior to freezing, the structural relaxation times follow an Arrhenius temperature dependence and the equimolar mixture shows typical liquid dynamics.
In the solid phase, there is substantial defect motion in the high-temperature crystal, during both the heating and cooling traverses. During heating, defects appear at $T = 0.9$, initially due to small-particle motion, but at later times also involving large-particle motion. This reduced large-particle mobility contrasts with the frozen crystal in which the small and large particles have almost identical mobilities. The structural and dynamic data for the heating traverse is consistent with a transition from rigid S1 crystal to crystal with defect motion to normal liquid and vice versa for the cooling traverse.

In contrast, the non-equimolar mixture shows no sign of crystallisation or phase separation upon cooling from the liquid state. The low temperature local structure is dominated by square S04 small particle environments, and L25 large particle environments. Our results suggest that approximately 50% of large particles find themselves in vertices of type (c) and (d), with another 10-20% each in vertices of type (b) and (e), where the vertex types refer to those in Figure 5.1. Although only 3% of particles find themselves in pentagonal S05 environments, these appear sufficient to disrupt the formation of long-range 12-fold orientational order. The changes in dynamic properties upon cooling below $T = 0.7$ - the rapid increase in structural relaxation times; the appearance of a plateau in the incoherent scattering functions and MSDs; the non-Arrhenius temperature dependence of the structural relaxation times and inverse diffusion constants at low temperature; and the onset of non-Gaussian dynamics - show behaviour typical of supercooled glass-forming liquids. Since our structural analysis found no development of long-range translational or orientational order, or tendency to crystallise or phase separate, we conclude that the non-equimolar mixture is a good glass-former.

This behaviour is rather surprising, as the model parameters are almost ideal for the formation of local square and triangular structures with the ability to tile space. It is also surprising given that a periodic structure with similar composition undergoes a first-order melting transition when heated from the solid state. We have not looked at heating a solid structure corresponding to an ideal random tiling - due to the time constraints of this project and the non-trivial problem of constructing such a configuration - but we suspect that it would also undergo a discontinuous transition to the liquid state despite its lack of long-range translational order. So is there another reason for the glass-forming ability of the non-equimolar mixture? The dynamics indicate that the liquid is supercooled below $T = 0.7$, and the equilibration
runtimes remain sufficiently long for both the intermediate scattering functions and non-Gaussian parameters to decay to zero above $T = 0.45$ (which is when the system falls out of local equilibrium). And yet a substantial fraction of non-ideal packings remain at $T = 0.5$, which ultimately are sufficient to disrupt the formation of long-range orientational order. Perhaps these defects are stabilised because the particle numbers that we have chosen cannot form an ideal random tiling that fits perfectly into a square simulation cell. In this case, the absence of larger domains with ideal 12-fold orientational order indicates that the random tiling structure is not substantially favoured relative to the amorphous structure.

Many models of glass-formers are based on particle interactions that encourage local ordering that cannot pack to fill space, for example the Dzugutov model [208]. In comparison to these, the non-equimolar mixture is noteworthy because it extends glass-formation to a model in which the interparticle potentials favour local ordering that can pack to fill space. In this latter case, it appears to be the large configurational entropy of the solid state that stabilises the amorphous state. Recall that we have chosen the composition that can decorate a square-triangle tiling ratio with maximal configurational entropy. In addition, this work suggests that metal alloys that form quasicrystals may also be good glass-formers, and that their structures may be related. Certainly, there is evidence for nanoquasicrystalline materials [183], and amorphous to quasicrystal transitions are often observed in metallic glasses upon devitrification [185].

The low temperature dynamics of the non-equimolar system are also interesting. The structural relaxation times of the small and large particles remain equal at all temperatures and the diffusion constants are equal until $T = 0.7$, below which they diverge slightly. This coupling of mobility and relaxation of both species in the present system may be explained by the lack of small particle nearest neighbours, since this implies that for a small particle to move or for its local structure to change, a large particle must also move. Structural relaxation of both particle species is also coupled in the equimolar mixture. The low-temperature dynamics of the non-equimolar mixture are also interesting. While we have not presented the results here, videos of the low-temperature particle motion (below $T = 0.5$) show that the main mechanism for motion is via a local distortion that allows a small particle to move from a square S04 environment into a neighbouring triangle of large particles, thus converting the initial square S04 environment into a triangular tile and the initial
triangular packing into a square S04 tile. This mechanism appears to be enhanced by nearby defects, e.g. S05 environments. This would also explain the enhanced mobility of small particles relative to large particles at low temperature. Kawamura [195] and Henley et al. [155, 159] both describe the minimum rearrangement that must take place to convert one ideal random square-triangle tiling into another. This involves the motion of at least 6 small and 6 large particles and is thus expected to have a high activation energy. Therefore the significant motion, and mechanism, that we observe at low temperature strongly suggests that the activation energy for structural rearrangements is significantly lowered in the presence of non-ideal packings. These may therefore be entropically stabilised.
Chapter 6

The Asymmetric H2 Crystal and a Chemically Ordered Glass ($\sigma_{12} = 1.1$)

We study the structure and dynamics of both equimolar and non-equimolar mixtures with $\sigma_{12} = 1.1$ in the fluid-solid phase region. The equimolar liquid is relatively stable to supercooling but eventually freezes into a substitutionally ordered crystal with an elongated hexagonal unit cell. Both heating and cooling traverses are characterised and the process of crystallisation is investigated. In contrast, the non-equimolar mixture shows no sign of crystallisation and forms an amorphous solid state when cooled. We argue that this system is a good glass-former and structurally distinct from the model with additive interparticle potential that was investigated in Part I.

6.1 Introduction

Although highly metastable to supercooling, the equimolar mixture of the present model eventually forms a crystal phase that can be described as a tiling of the plane by unit cells consisting of two small particles surrounded by six large particles in an elongated hexagonal arrangement. This unit cell, illustrated in Figure 6.3(a), has previously been described by Likos and Henley [155], who investigated the phase diagram of binary hard-disc mixtures but did not perform any simulations. We will follow their convention and refer to the local hexagonal unit as the H2 unit cell and the crystal as the H2 crystal. A 2D binary Lennard-Jones (LJ) mixture studied in the context of quasicrystal stability also has the H2 crystal as one of its ground states [161], however this LJ model has substantially different interactions lengths and
forms structures not observed in the present system. We characterise the structure and dynamics of the equimolar mixture in Section 6.3.

The non-equimolar mixture (with composition \( x_1 = 0.3167 \)) is noteworthy for its ability to form an amorphous solid that is structurally more homogeneous than the equimolar model studied in Part I, despite over two-thirds of its components being of the same species. It also has less diversity of local coordination environments and a medium-range order that can be described in terms of favoured packings of local environments. Surprisingly, it shows little sign of the H2 crystal order present in the equimolar liquid, with dynamic behaviour that is typical of other glass-forming liquids. We characterise the structure and dynamics of this system in Section 6.4.

While the main object of the present study is to characterise the changes in phase behaviour and dynamics that occur as the interparticle potential \( \sigma_{12} \) is varied, we also spend some time in this chapter studying the process of crystallisation in the equimolar mixture. This work is presented in Section 6.3.4. This is not meant to form a comprehensive study of nucleation and crystallisation, but rather to demonstrate that non-additive soft-disc mixtures may serve as useful model systems for such work.

To put this into context, we give a brief introduction to the study of crystallisation in the remainder of this section.

Crystal nucleation is an important phenomenon in many processes, yet scientific understanding of its molecular mechanism remains incomplete. Despite progress, many open questions concerning crystallisation phenomena still remain, including the rate of formation of the crystal phase, structure and composition of the critical nucleus, role of solvents and foreign objects etc. Crystals can take many forms, only one of which is the most stable. However it is usually not known in advance which structure will form upon nucleation. Ostwald’s rule of stages [209] states that the crystal phase that nucleates from a supercooled liquid is the one that is closest to the liquid state in its free energy. Hence crystallisation via nucleation may yield the metastable form instead of the most stable structure. This issue is particularly important, for example, in the pharmaceutical industry where the same drug molecule can have different properties due to differences in its crystal structure.

A fundamental understanding of the nucleation, growth kinetics, and morphology of crystals grown from the melt requires a detailed microscopic description of the crystal-melt interface [210–213]. However, such information is difficult to obtain experimentally. For example, it is difficult to detect the presence of small nuclei, and it
is difficult to probe the crystal-melt interface, especially at the high melting/freezing temperatures typical of metal alloys. Not surprisingly, computer simulations have played a leading role in the determination of the microscopic structure, dynamics, and thermodynamics of such systems [214]. The majority of simulation studies so far have focused on single component systems, ranging from simple models such as hard spheres [214–217] or Lennard-Jones [218, 219] to more ‘realistic’ systems, such as water [220–222], silicon [223, 224] or simple metals [225, 226]. In contrast, there have been relatively few studies of multicomponent systems [152, 227–232], despite the reality that most materials of technological interest are mixtures (for example, doped semiconductors, alloys, and intermetallic compounds).

We therefore suggest that the ordered S1 and H2 crystal phases, characterised in this chapter and in Chapter 5, offer valuable models systems in which to further our understanding of crystallisation. These non-additive soft-disc mixtures have the added complexity of two particle species with the simplicity of two dimensions and purely repulsive potentials. They may also be viewed as model systems for the study of ordering in monolayers. We are not aware of any previous studies of ordered crystals, crystallisation or glass-formation in non-additive soft-disc mixtures, nor of any studies of ordered crystals or crystallisation in additive soft-disc mixtures.

The rest of this chapter is structured as follows. In Section 6.2 we describe the model and computational methods used. We characterise the structural and dynamic properties of the equimolar mixture in Section 6.3 and, in Section 6.3.4, study the process of crystallisation for this system. Our study of glass-formation in the non-equimolar mixture is presented in Section 6.4. This is followed by a summary of the main results and a comparison of the structure and phase behaviour of the two mixtures in Section 6.5.

### 6.2 Model and Computational Details

We consider a 2D system consisting of a binary mixture of particles interacting via purely repulsive potentials of the form

\[
    u_{ab}(r) = \epsilon \left( \frac{\sigma_{ab}}{r} \right)^{12} \tag{6.1}
\]

where \(\sigma_{12} = 1.1 \times \sigma_{11}\) and \(\sigma_{22} = 1.4 \times \sigma_{11}\). All units quoted will be reduced so that \(\sigma_{11} = \epsilon = m = 1.0\) where \(m\) is the mass of both types of particle. Specifically, the
A total of $N = 1440$ particles were enclosed in a square box with periodic boundary conditions.

The molecular dynamics simulations were carried out at constant number of particles, pressure ($P = 13.5$) and temperature using the Nosé-Poincaré-Andersen (NPA) algorithm developed by Laird et al. [83, 84]. This algorithm is discussed further in Appendix A, where we also list the equations of motion in 2D. The equations of motion were integrated using a generalised leapfrog algorithm [84]. The time step employed was $0.05\tau$ for $T > 1$, and $0.01\tau$ for $T \leq 1$. For argon units of $\eta = 120k_B$, $m = 6.6 \times 10^{-23}g$ and $\sigma_{11} = 3.4\text{Å}$, these time steps correspond to approximately 10 and 20 femtoseconds respectively.

A non-equimolar mixture consisting of $N_1 = 456$ small particles and $N_2 = 984$ large particles (giving $x_1 = 0.3167$ to 4 sig. fig.) was studied at 16 different reduced temperatures from $T = 5$ to $T = 0.2$. The starting configuration of the run at $T = 5$ was an equilibrated configuration at $T = 5$ for the equimolar system described in this chapter with the appropriate number of small particles changed to large particles. The starting configuration of each lower temperature equilibration run came from the final configuration of the preceding higher temperature run. For $T \geq 0.45$, the equilibration times were longer than the times taken for all the dynamic correlation functions investigated to decay to less than 0.1. Below $T = 0.45$ the system is no longer able to reach equilibrium within the finite time scale of the simulations. Thus, the computer glass transition temperature for these simulations, defined as the temperature at which the system falls out of equilibrium, lies between $T = 0.45$ and $T = 0.4$. At all temperatures the equilibration runs were taken out until steady state was achieved, i.e. until the average thermodynamic properties remained constant in time. Table C.15 (in Appendix C.4) lists the temperatures of each state studied as well as the equilibration and production times. The final configurations of the equilibration runs were used to start the production runs, and the ‘masses’ of the Anderson piston and Nosé thermostat (see Appendix A) were $Q_v = 0.002$ and $Q_s = 1000$, respectively, for all temperatures.

Both cooling and heating traverses were studied for the equimolar mixture (with $N_1 = 720$ small particles and $N_2 = 720$ large particles). Tables C.9 and C.10 (in Appendix C.3) list the temperatures of each state studied as well as the equilibration and production times for the cooling and heating traverses, respectively. Full production runs were not performed for cooling runs at $T < 0.6$ and heating runs at
6.3 Metastability and Freezing of the Equimolar Mixture

$T > 0.7$. In these cases the thermodynamic averages were calculated during the latter part of the equilibration run after there was no further change in average properties. These ‘production’ runs are indicated by an asterisk (*) after the production runtime. No further properties, structural or dynamic, were calculated at these temperatures. The initial configuration for the cooling traverse was a previously equilibrated configuration at $T = 5$, while the initial configuration for the heating traverse was the constructed periodic structure shown in Figure 6.2(e). The starting configurations for production runs and for lower (or higher) temperature equilibration runs are as described above for the non-equimolar mixture. For the cooling traverse, the ‘masses’ of the Anderson piston and Nosé thermostat were $Q_v = 0.0002$ and $Q_s = 1000$, respectively, for all temperatures. For the heating traverse, we used $Q_v = 0.0002$ for $T \leq 0.62$ and $Q_v = 0.000001$ for $T \geq 0.64$, and $Q_s = 10$ for $T \leq 0.2$ and $Q_s = 1000$ for $T \geq 0.3$. At low temperatures the kinetic energy fluctuations for the crystal phase became regular unless $Q_s$ was reduced, and at high temperatures the density fluctuations became regular unless $Q_v$ was reduced. We note that changing $Q_s$ and $Q_v$ generally has little effect on the thermodynamic averages, except near a critical point where increasing the size of the fluctuations can cause one phase (usually the solid) to become unstable with respect to the other.

6.3 Metastability and Freezing of the Equimolar Mixture ($x_1 = 0.5$)

6.3.1 Thermodynamic Properties

For reference, thermodynamic averages are listed in Table C.9 for the cooling traverse, and in Table C.10 for the heating traverse. The isobaric phase diagram for the equimolar mixture is shown in Figure 6.1 for $T < 1.1$. Upon cooling, the density increases smoothly at a greater than linear rate. Given sufficient time, the system crystallises at $T = 0.6$ into a labile crystal, a representative configuration of which is shown in Figure 6.2(d). The density of this defected crystal is indicated by the filled diamond in the isobaric phase diagram (Figure 6.1). Heating of the crystalline configuration shown in Figure 6.2(e) reveals a hysteresis region in the isobaric phase diagram extending from $T = 0.6$ to $T = 0.8$. This is very large compared to the hysteresis regions observed for freezing/melting in the single-component soft-disc system.
at the same pressure and for the S1 crystal phase studied in Chapter 5. For the former, the region extends from $T = 0.95$–$0.98$, and for the latter, it extends from $T = 1.02$–$1.06$. We have heated the defective crystal shown in Figure 6.2(d) and found that melting occurs at $T = 0.7$ but not at $T = 0.68$. The true thermodynamic melting/freezing temperature should therefore lie somewhere in the range $T = 0.69$–$0.8$. The apparent high metastability of the liquid phase to supercooling is investigated in the following work. We also study the process of crystallisation at $T = 0.6$.

In the next section we characterise the changes in structure that occur during heating and cooling of the equimolar mixture. Note that structural properties have only been calculated for the heating traverse in the range $T = 0.1$–$0.7$.

### 6.3.2 Development of Crystalline Order

**Particle Configurations**

Representative particle configurations from the cooling and heating traverses are shown in Figure 6.2. We draw attention to several important features. The small
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Figure 6.2: Representative particle configurations: during cooling at (a) $T = 1$, (b) $T = 0.6$ before freezing, (c) $T = 0.6$ during freezing, and (d) $T = 0.6$ after freezing; and during heating at (e) $T = 0.1$ and (f) $T = 0.8$. The small and large particles are represented by filled and open circles respectively.
and large particles species appear to be well-mixed at all temperatures, consistent with an effective attraction between unlike particle species. During cooling, the initially disordered liquid (a) appears to develop large quantities of crystalline-like order (b) prior to freezing. The crystal that is formed consists of elongated hexagonal unit cells, of the type illustrated in Figure 6.3(a), that we will refer to as H2 unit cells. These pack together in both parallel and near-perpendicular (herringbone-like) arrangements, as represented schematically in Figure 6.3(b)-(c).

The structure of the growing crystal appears to be quite labile; some of the herringbone packing present during crystallisation [Figure 6.2(c)] has changed to parallel packing by the time the main crystallisation event is complete (d). There are still small amorphous regions in (d). A perfect crystalline configuration of parallel-packed H2 cells fits well into a square simulation box and was used for the heating traverse. The constructed crystal (e), with all unit cells packed in a parallel fashion, is stable right up to $T = 0.8$ (f), the only defects present being a couple of substitutions and some herringbone packing in the upper right-hand corner. We note that because the H2 unit cells are able to pack together in both parallel and herringbone alignments without constraints on the periodicity of these, it is theoretically possible for this system to form a solid state with perfect H2 local order, and long-range orientational order, yet lacking in long-range translational order. The relative stability of such configurations could be investigated by using a simulation algorithm that allows for
the box shape to change, for example that of Melchionna et al. [233].

Pair Distribution Functions

The pair distribution functions (PDFs), defined in Section 5.3.2, describe the radially averaged structure about particles. The PDFs for the cooling traverse are plotted in Figures 6.4 and 6.5. Also shown, for comparison, are the respective PDFs at $T = 0.6$ during the heating traverse. For reference, the complete PDFs for the heating traverse are plotted in Figures C.3 and C.4.

Figure 6.4: The partial pair distribution functions $g_{11}(r)$ and $g_{22}(r)$ for the cooling traverse as a function of distance from $T = 5$ down to $T = 0.6$. For $T \leq 3$, each curve has been shifted upwards by one unit from the higher temperature curve directly preceding it. For comparison, the respective functions at $T = 0.6$ during the heating traverse have also been plotted.
Upon cooling, the liquid shows increasing local ordering until at $T = 0.6$ there are undulations in the PDFs out to $r = 8\sigma_{11}$. The initial peak structure is similar to that in the solid-state PDFs at the same temperature, but there are significant differences beyond $r = 2.5\sigma_{11}$. For example, the fourth peaks in the crystalline partial pair distribution function (PPDFs) are absent in the liquid state PPDFs. Therefore, whatever crystalline order is present in the liquid prior to freezing must be in very small domains or involve herringbone packing, as the latter would result in a different peak structure to the parallel-packed crystal used for the heating traverse.
The partial structure factors were calculated from the PPDFs, using the method explained in Section 5.3.2. They are plotted along with the total structure factor in Figures C.5 and C.6. We did not investigate structural relaxation in the solid-state and have therefore not calculated structure factors for the heating traverse.

We further investigate the local order in the liquid and solid states using a number of measures built upon nearest neighbour interactions. Two particles of type $a$ and $b$ are defined to be nearest neighbours if they are separated by a distance less than $cut_{ab}$, where $cut_{ab}$ is the distance at which the first minimum in the respective partial PDF, $g_{ab}(r)$, occurs. For reference, cutoff distances obtained for the cooling and heating traverses are listed in Tables C.11 and C.12, respectively.

**Local Structure Parameters**

In Figure 6.6 we plot the distribution of local packing environments as a function of temperature. The main change during the cooling traverse is a rapid increase in the fraction of L43 and S14 environments below $T = 1$; by the time freezing

![Figure 6.6](image)

**Figure 6.6:** The distribution of local packing environments as a function of temperature. We have identified a particular neighbourhood with the following notation: A small particle with $m$ small neighbours and $n$ large neighbours is designated as $S_{mn}$ and the analogous large particle is indicated as $L_{mn}$.
commences, over half the particles are in these environments. Analysis of the H2 crystal (both parallel and herringbone packings) shows that all the small particles have S14 environments and all the large particles have L43 environments. Therefore, these results indicate that there may be a high degree of crystalline order in the low-temperature liquid phase. As expected, the solid phase during the heating traverse is composed almost entirely of L43 and S14 environments. Above $T = 0.6$, there is a small decrease in the fraction of these environments that is most likely due to vibrational distortions, as substitutional defects do not appear until $T = 0.7$.

To resolve to what extent the S14 environments pack together to form H2 unit cells [see Figure 6.3(a)], we consider the fraction of particles in H2 cells $f_{H2}$ as a function of temperature. An H2 cell is defined as a small particle with S14 local environment whose neighbouring small particle also has the S14 local environment. Figure 6.7(a) clearly demonstrates that $f_{H2}$ also rises rapidly prior to freezing. In contrast, the distribution of nearest neighbour interactions $n_{ab}$ between particles of type $a$ and $b$, plotted in Figure 6.7(b), shows relatively little change with temperature. From these results we conclude: (i) that the liquid has a high degree of crystalline-like local structure prior to freezing; and (ii) that the dominant change in local structure on cooling is a change in the topology (spatial distribution) of nearest neighbour interactions, rather than a change in their relative abundance.
Orientational Order Parameters

To investigate the orientational correlation between H2 cells, we define a new set of order parameters. The ‘orientation’ of an H2 cell $\theta_{H2}$ is defined as the angle subtended by the $x$-axis and the line running through the two small particles in the H2 cell, in the range $0^\circ \leq \theta_{H2} < 180^\circ$. And the ‘location’ of the H2 cell $r_{H2}$ is defined as the midpoint of the line joining the two small particles. See Figure 6.3(a) for a graphical representation of these quantities. Using them, we define an orientational distribution function for H2 cells as

$$P_{H2}(\theta) = \left\langle \frac{1}{N_{H2}} \sum_{j} \theta_{H2,j} \delta(\theta - \theta_{H2,j}) \right\rangle,$$

(6.2)

where $N_{H2}$ is the total number of H2 cells, $\theta_{H2,j}$ is the orientation of the $j$th H2 cell, and the angular brackets denote an average over different configurations in time.

We also define a pair distribution function for H2 cells as

$$g_{H2}(r) = \left\langle \frac{1}{N_{H2}\rho_{H2}} \frac{N_{H2}N_{H2}}{2} \sum_{j=1}^{N_{H2}} \sum_{k\neq j} \delta[r - r_{H2,ij}] \right\rangle,$$

(6.3)

where $N_{H2}$ is the total number of H2 cells, $\rho_{H2} = V/N_{H2}$, $r_{H2,ij} = |r_{H2,i} - r_{H2,j}|$ is the separation between the $i$th and $j$th H2 cells, and the angular brackets denote an average over different configurations in time.

We test for the presence of long-range orientational correlation between H2 domains by defining an orientational correlation function as

$$C_{H2}(r) = \left\langle \frac{1}{N_{H2}\rho_{H2}} \frac{N_{H2}N_{H2}}{2} \sum_{j=1}^{N_{H2}} \sum_{k\neq j} \cos[2(\theta_{H2,j} - \theta_{H2,k})] \delta(r - |r_{H2,j} - r_{H2,k}|) \right\rangle,$$

(6.4)

where the angular brackets again indicate an average over time origins. This orientational correlation function is weighted by the translational correlations. To see it free of this bias we plot the ratio $G_{H2}(r) = C_{H2}(r)/g_{H2}(r)$. If all the H2 cells at a given separation $r$ lie parallel to each other then $G_{H2}(r) = 1$, while if they all lie perpendicular to each other then $G_{H2}(r) = -1$.

In Figure 6.8 we plot the distribution of H2 cell orientations during the cooling and heating traverses. Plot (b) shows that during the heating traverse the H2 cells remain in a parallel alignment perpendicular to the $x$-axis, as indicated by the peak.
Figure 6.8: The temperature dependence of the distribution of H2 cell orientations during the (a) cooling and (b) heating traverses. The absolute value of the fraction depends upon the size of the binning over angles and is therefore unimportant. For clarity, each curve in (a) below $T = 5$ has been shifted upwards by 0.01 units above the higher temperature curve directly preceding it, and each curve in (b) above $T = 0.1$ has been shifted upwards by 0.01 units above the lower temperature curve directly preceding it.
around $\theta_{H_2} = 90^\circ$. As the temperature increases the peak broadens, presumably due to vibrational motion. We find no evidence of herringbone packing in the temperature range studied. In contrast, during cooling [plot (a)], there is no strong alignment of H2 cells. Some small undulations appear below $T = 0.68$, often separated by an angle around $80^\circ$, but it is clear that the majority of H2 cells are not aligned with respect to each other.

The orientational correlation functions $G_{H_2}$ for the cooling traverse are plotted in Figure 6.9(a). Also shown for comparison - plot (b) - are the pair distribution functions $g_{H_2}(r)$ at $T = 0.6$ during both heating and cooling traverses. Note that $C_{H_2}$ for the heating traverse is almost identical to $g_{H_2}(r)$ since all H2 cells are parallel to one another; $G_{H_2}$ for the heating traverse therefore contains no additional information and has not been plotted. We find that during the heating traverse there is clear long-range structure in $g_{H_2}(r)$ extending the full length of the simulation cell. An example at $T = 0.6$ is shown in plot (b). In contrast, there is no long-range orientational order between H2 cells during cooling. There is, however, increasing structure at small separations as the temperature is reduced. The maxima in $G_{H_2}(r)$ near $r = 2.2, 2.8, 3.5$ and 4.5 match the expected nearest and next-nearest neighbour separations of H2 cells in perfect parallel packing, and also appear as sharp peaks in $g_{H_2}(r)$ during the heating traverse. We therefore conclude that these are due to the presence of small clusters of H2 cells packed in parallel. Furthermore, the minima in $G_{H_2}(r)$ around $r = 2.5$ and 4.0 match the expected nearest and next-nearest neighbour separations of H2 cells in herringbone packing, and also appear as additional peaks in $g_{H_2}(r)$ during the cooling traverse that are absent during the heating traverse. The near-perpendicular alignment of H2 cells in herringbone packing would also explain the negative values of these minima. We therefore conclude that in the liquid phase below $T = 0.7$ there are clusters of aligned H2 cells that are 3–4 H2 units across. The increasing fluctuations at higher temperature indicate poor statistics, probably due to the increasingly small number of H2 cells in the sample.

This result, along with the increase in the fraction of particles in H2 order and the lack of any strong angular preference for H2 cells, suggests that before freezing commences there is a significant amount of H2 order in small domains that are unaligned with respect to each other.

We also tested for the presence of 4-, 6- and 12-fold orientational order in the system (see Section 5.3.2 for the definition of the orientational order parameters).
Figure 6.9: (a) The temperature dependence of the orientational correlation function for H2 cells $G_{H2}(r)$ during the cooling traverse. (b) The pair distribution function for H2 cells $g_{H2}(r)$ at $T = 0.6$ during the cooling and heating traverses. For clarity, functions have been offset vertically from each other.
6.3 Metastability and Freezing of the Equimolar Mixture

The temperature dependence of the bulk averaged $n$-fold order parameters $\Psi_n$, where $n = 4, 6, 12$, and their small ($\Psi_{n,1}$) and large ($\Psi_{n,2}$) particle contributions, for the cooling and heating traverses. The filled symbols indicate data from the heating traverse.

The bulk averaged $n$-fold order parameters $\Psi_n$ are plotted in Figure 6.10 for both the heating and cooling traverses. The major change upon cooling is a decrease in 6-fold order below $T = 1$. This is likely caused by the rapid increase in 5-coordinated S14 environments and 7-coordinated L43 environments (see Figure 6.6), which must also explain the discontinuity in the bulk 6-fold order between the liquid and solid phases. The increase in $\Psi_{4,1}$ below $T = 1$ must also be related to the increase in S14...
environments, as $\text{SO}_4$ environments make up less than 2% of the total. The changes in 12-fold order are likely due to the changes in 4- and 6-fold orientational order.

The $n$-fold orientational correlation functions $G_n(r)$ test for long-range orientational correlation of the local $n$-fold domains. During the cooling traverse, we find that $G_{4,1}(r)$, $G_{6,1}(r)$ and $G_{6,2}(r)$ develop very weak correlations (out to $r = 5\sigma_{11}$). The peak structure of these functions is very similar to that observed at small $r$ during the heating traverse (for which $G_{4,1}(r)$, $G_{6,1}(r)$ and $G_{6,2}(r)$ have very weak long-range correlations). We therefore conclude that the 4- and 6-fold orientational correlations observed in the liquid phase are simply a reflection of the H$2_\text{O}$ order in the system, and do not include these plots.

At low temperatures, the liquid phase contains a very high degree of local crystalline-like order, with over 50% of particles in H$2_\text{O}$ unit cells. However, these cells appear only to form small clusters, usually less than 3 units across, that remain unaligned with respect to each other.

### 6.3.3 Dynamics and Structural Relaxation

In this section, we present an analysis of the changes in particle transport and structural relaxation that occur upon cooling of the equimolar mixture.

#### Intermediate Scattering Functions and Arrhenius Plot

For the equimolar mixture, we have calculated the incoherent (or self) intermediate scattering functions $F_{s,1}(k,t)$ and $F_{s,2}(k,t)$ for the small and large particles, respectively (see Section 5.3.3 for their definitions). $F_{s,1}(k,t)$ and $F_{s,2}(k,t)$ have been measured at the positions of the first maxima in the static structure factors $S_{11}(k)$ and $S_{22}(k)$, which are weakly dependent on temperature and are listed in Table C.13. Log-linear plots of the self intermediate scattering functions are shown in Figure 6.11. The relaxation curves broaden with decreasing temperature and, below $T = 0.7$, develop an increasingly prominent shoulder near $10\tau$. The appearance of a shoulder in the intermediate scattering function is often a sign of supercooled liquid behaviour. For example, glass-formers typically develop two-step relaxation functions upon supercooling as discussed in Section 1.2. Interestingly, $F_{s,1}(k,t)$ and $F_{s,2}(k,t)$ decay at almost the same rate at a given temperature.

The structural relaxation time $\tau_{e,1}$ is defined as the time taken for the incoherent scattering function $F_{s,1}(k,t)$ to decay to $1/e$. The temperature dependence of
6.3 Metastability and Freezing of the Equimolar Mixture

Figure 6.11: The incoherent scattering functions $F_{s,1}(k_1, t)$ and $F_{s,2}(k_2, t)$ for the small and large particles, respectively. The wave vectors $k_1$ and $k_2$ are the first peak positions in the respective partial structure factors (listed in Table C.13). From left to right the temperatures of the curves are $T = 5$, 3, 2, 1, 0.9, 0.8, 0.7, 0.68, 0.66, 0.64, 0.62, and 0.6. Note the appearance of a shoulder in the curves below $T = 0.7$.

This relaxation time, plotted in Figure 6.12, is Arrhenius at high temperatures, but diverges weakly from Arrhenius behaviour as the temperature drops below $T = 0.7$. This deviation from Arrhenius behaviour also resembles the dynamic behaviour of supercooled fragile glass-formers. Similarly, the diffusion constants - measured in the region where the mean-squared displacement (MSD) has reached its long-time constant value ($R_2^2(t) > \sigma_{11}$) - also show a strong deviation from Arrhenius temperature dependence, with the onset of this deviation occurring just below $T = 0.7$. The diffusion constants for the small and large particle species remain approximately equal at all temperatures. For reference, the MSDs are plotted in Figure C.7, and the structural relaxation times and diffusion constants are listed in Table C.14.
Figure 6.12: Arrhenius plot of the structural relaxation time $\tau_{e,1}$ and the inverse diffusion constants $D_{1}^{-1}$ and $D_{2}^{-1}$. The dashed lines are linear regressions through the data for $T > 0.7$. Note the divergence from Arrhenius behaviour at low temperatures.

Non-Gaussian Parameter

As explained in Section 5.3.3, the non-Gaussian parameters $A_{a}(t)$ can be used as a measure of the degree of dynamic heterogeneity in a sample. Large values at intermediate times can be attributed to a broad distribution of local mobilities. The non-Gaussian parameters for the present system are plotted in Figure 6.13. A rapid rise in non-Gaussian behaviour is observed at low temperatures for both the large and small particle species; the trend is for the maxima to move to longer times as they increase in height. Given that we found no evidence of crystallisation during these runs, we attribute the non-Gaussian behaviour to an increasing heterogeneity in the liquid dynamics at intermediate times. Furthermore, at all temperatures the non-Gaussian parameters appear able to decay to zero over the timescale of the equilibration runs, indicating that the equilibration times were long with respect to structural relaxation.
Figure 6.13: The non-Gaussian parameter averaged over all particles, $A(t)$, and averaged over small and large particles, $A_1(t)$ and $A_2(t)$, respectively. The temperatures of the curves are as listed in Figure 6.11. Observe the rapid increase in the peak heights with decreasing temperature.
Upon cooling below $T = 0.7$, the liquid phase increasingly shows dynamic behaviour typical of a supercooled liquid; the diffusion constants and structural relaxation times deviate from Arrhenius behaviour, the non-Gaussian function develops an increasingly large peak at intermediate times, and a shoulder appears in the intermediate scattering function. The observation that the defected H2 crystal melts near $T = 0.7$ also suggests that the thermodynamic melting/freezing temperature $T_f$ lies somewhere near this temperature. Yet the liquid remains stable to crystallisation over equilibration times that are sufficiently long for the average particle to travel $5–10\sigma_{11}$, and for all the particles to randomise their initial kinetic state (the non-Gaussian function decays to approximately zero). We investigate the origin of this metastability further in the next section, by studying the process by which crystallisation eventually proceeds.

### 6.3.4 Alignment of Unit Cells During Crystallisation

As discussed in the Section 6.1, the mechanism by which crystallisation proceeds in substitutionally ordered crystals appears to have received relatively little attention. In this section we present a brief investigation into the process of crystallisation in the H2 system. In particular, we wish to uncover the rate-limiting step in order to gain some insight into the large metastability of this system to supercooling despite the high degree of crystalline order in the liquid. We also propose a reason for the relatively slow process by which crystallisation eventually proceeds.

We consider several properties investigated above, as well as a number of new measures of H2 unit cell aggregation, and study the change in these properties before, during and after crystallisation over the course of a $50,000\tau$ run. The starting configuration for this run was the final configuration of the $10,000\tau$ equilibration run at $T = 0.6$.

In Figure 6.14 we plot the change in several thermodynamic properties as a function of time. The quantities undergo large fluctuations but some clear trends can be observed. After about $6,000\tau$ the fraction of nearest neighbour interactions between different particle species $n_{12}$ starts to increase. Soon after, the density $\rho$ starts to increase. Both $n_{12}$ and $\rho$ increase fairly continuously until about $28,000\tau$ after which time they return to fluctuations about a constant value. In contrast, the potential energy (PE) shows only a small change relative to the magnitude of its fluctuations. Therefore, the crystallisation process appears to last from about $6,000–28,000\tau$, and
Figure 6.14: The change in volume, density, $n_{12}$ and potential energy as a function of run time before, during and after crystallisation at $T = 0.6$.

does not commence until $16,000\tau$ after the start of equilibration at $T = 0.6$.

Figure 6.15 shows the change in H2 cell orientation and the fraction of particles in H2, S14 and L43 local order during the run; and Figure 6.16 shows the change in the number of H2 clusters, the mean number of particles per H2 cluster, and the distribution of cluster sizes over the duration of the run. We define the mean number of particles per H2 cell as the total number of particles in H2 cells divided by the total number of H2 cells. When H2 cells pack together they share particles, the result being that the mean number of particles per H2 cell decreases. This therefore provides a measure of the degree to which H2 cells cluster together. We also calculate the total number of H2 clusters and the distribution of cluster sizes. Two H2 cells with indices $i$ and $j$ are defined as belonging to the same H2 cluster if $|\mathbf{r}_{H2,i} - \mathbf{r}_{H2,j}| \leq 3.1$, where $r = 3.1$ is the position of the minimum between nearest and next-nearest neighbour peaks in $g_{H2}(r)$.

From $0–10,000\tau$, the size of the largest H2 cluster undergoes large fluctuations
Figure 6.15: The change in (a) the distribution of H2 cell orientations, and (b) the fraction of particles in H2 unit cells and in S14 and L43 local environments, as a function of run time before, during and after crystallisation at $T = 0.6$. For clarity, the curves in (a) have been displaced vertically from each other.

between 25 and 105 particles, before jumping to a size of 125 particles from which growth proceeds. The critical nucleus therefore appears to be around 115 particles in size. However, simply reaching a critical cluster size cannot be what is responsible for
initiating crystallisation. The number of particles in H2 order (and in S14 and L43 order) starts to increase around 7,000\(\tau\), i.e. before the largest cluster has exceeded 115 particles, and even after crystallisation has begun the largest cluster size drops below 115 particles. The angle distribution of H2 cells supplies the answer. At 0\(\tau\) the angle distribution is very broad with no clear peaks, but after 5,000\(\tau\) two small peaks near 65° and 140° are now visible. By 10,000\(\tau\) more clustering of angles is apparent, which with time form two peaks separated by an angle of about 80°, consistent with the development of herringbone packing of H2 cells. There is also a small decrease in the mean number of particles per H2 cell around 6,000\(\tau\), indicating a small increase in the clustering of H2 cells at this time. Small drops in the total number of clusters and in the mean number of particles per H2 cell near 10,000\(\tau\) are consistent with a larger growth event involving the aggregation of two smaller (aligned) clusters. This scenario is supported by the lack of an equivalent sudden increase in the number of particles in H2 order near 10,000\(\tau\). We therefore conclude that the rate limiting step

\[ \text{Figure 6.16: } \text{The change in the clustering of H2 cells as a function of run time before, during and after crystallisation at } T = 0.6. \]
Figure 6.17: (a) The hexagonal H2 unit cell is related to two square S1 unit cells via a simple distortion. (b)-(c) Different crystalline packings of H2 cells can interconvert via distortions like the one illustrated in (a). (d) H2 cells can also stack together in ‘frustrated’ packings that cannot grow to fill space. The filled and open circles represent small and large particles, respectively, and the thick line represents the H2 and S1 unit cells.

is the alignment of H2 cells. Once sufficient cells become aligned, the fraction of crystal-like local environments starts to increase, eventually resulting in aggregation of two or more existing aligned clusters.

Crystallisation is a slow process, lasting for at least $22,000\tau$, and appears to proceed irregularly. The size of the largest cluster again increases suddenly around $18,000\tau$ and $24,000\tau$. The former appears to be mainly a growth event (the number of particles in H2 order increases suddenly while the total number of clusters fluctuates about an approximately constant value), while the latter appears to be a combination of both growth ($f_{H2}$ increases) and aggregation (the total number of clusters decreases). These interpretations are supported by changes in the mean number of particles per H2 cell: as the cells aggregate, more particles become shared between H2 cells and the value decreases. Finally, we note that between $28,000\tau$ and $50,000\tau$, i.e. after the main crystallisation event appears to be complete, there is a shift from herringbone packing towards parallel packing of H2 cells; the peak in the H2 angle distribution function near $40^\circ$ grows while the peak near $125^\circ$ shrinks. Therefore, we conclude that the most stable packing is the parallel one, and suggest that the herringbone packing provides a kinetically favourable interface for crystal growth.
Figure 6.18: A configuration after a freezing transition at $T = 0.58$. Note the presence of grain boundaries between unaligned crystalline domains.

Figure 6.17 illustrates how different packings of H2 cells might interconvert via simple distortions. Small changes in particle position can convert an asymmetric H2 unit cell into two symmetric S04 environments, i.e. two S1 unit cells. Different S1 cells may then recombine resulting in interconversion between different parallel packings of H2 cells (b) or between parallel and herringbone packings (c). Of course, this interconversion may proceed in a step-like manner rather than all at once. Frame (d) illustrates one possible reason for slow crystal growth. H2 cells may pack together in arrangements that cannot grow to fill space.

Finally, while crystallisation occurs at $T = 0.6$ given sufficient time, the liquid phase is stable for long times even at lower temperatures. If, after $10,000 \tau$ equilibration at $T = 0.6$, the liquid is cooled to $T = 0.58$ it is stable for a further $10,000 \tau$ before crystallisation commences. And if cooled to $T = 0.56$ at this time it takes a further $12,000 \tau$ before crystallisation starts. At these lower temperatures, crystallisation appears to proceed simultaneously via several different nucleation events. Following crystallisation, the final structure, shown in Figure 6.18 for $T = 0.58$, consists of several unaligned crystalline domains separated by grain boundaries.

In summary, we conclude that the rate-limiting step for nucleation is the alignment of a sufficient number of H2 cells in an arrangement that can grow to fill space, i.e. either in herringbone or parallel packing of a combination of these. At $T = 0.6$,
growth then proceeds via the creation of new crystalline order in the liquid phase and the occasional attachment of existing crystalline clusters to the growing nucleus. In addition to the alignment of existing H2 cells, growth may be slowed via the compositional changes needed to create new crystalline local order and by false starts leading to packing of H2 cells in arrangements that cannot grow to fill space. Additionally, the growing crystal is quite labile, its structure interconverting between different parallel and herringbone packings. The interior of the final crystal is dominated by parallel packing which leads us to believe that this is the energetically preferred arrangement of H2 cells. At lower temperatures, there appear to be multiple nucleation events, resulting, at least initially, in a structure with many grain boundaries.

6.4 Glass-Formation in the Non-Equimolar Mixture \((x_1 = 0.3167)\)

6.4.1 Thermodynamic Properties

The isobaric phase diagram is plotted in Figure 6.19. The density increases smoothly with cooling, showing no sign of a first order phase transition. There is, perhaps, a small change in slope between \(T = 0.45\) and \(T = 0.4\), which coincides with the

![Figure 6.19](image-url)  

**Figure 6.19**: Isobaric \((P = 13.5)\) phase diagram. Error bars represent one standard deviation. Note that the density increases smoothly with cooling.
6.4 Glass-Formation in the Non-Equimolar Mixture

Temperature at which the system falls out of equilibrium. For reference, the thermodynamic averages for the potential energy per particle \(U\), energy per particle \(E\), enthalpy per particle \(H\), and number density per particle \(\rho\) are summarised in Table C.15 for the range of temperatures that were investigated.

6.4.2 Development of Short- and Medium-Range Order

Particle Configurations

Representative particle configurations are shown in Figure 6.20. There is little change in structure with temperature. The local structure becomes more regular upon cooling, but the small particles appear evenly dispersed throughout the sample at all

![Figure 6.20](image-url)

**Figure 6.20:** Representative particle configurations at (a) \(T = 1\), (b) \(T = 0.6\), and (c) \(T = 0.2\). The small and large particles are represented by filled and open circles respectively.
temperatures. Rather than forming large crystalline clusters, the large particles remain dispersed as the system is cooled.

**Pair Distribution Functions**

The pair distribution function (PDF) and the partial pair distribution functions (PPDFs), defined in Section 5.3.2, are shown for the non-equi molar mixture in Figures 6.21 and 6.22. Upon cooling, the PDFs develop structure over increasing lengthscales (out to about $6\sigma_{11}$), but there is clearly no long-range translational order in the system. There are some similarities to the PDFs calculated for the equimolar mixture.

**Figure 6.21:** The partial pair distribution functions $g_{11}(r)$ and $g_{22}(r)$ as a function of distance from $T = 5$ down to $T = 0.2$. For $T \leq 3$, each curve has been shifted upwards by one unit from the higher temperature curve directly preceding it.
but also some notable differences: $g_{11}(r)$ has a smaller first peak, indicating that there are less nearest neighbour contacts between small particles; $g_{12}(r)$ has an additional peak at $3.8\sigma_{11}$; and $g_{22}(r)$ has an additional peak at $2.4\sigma_{11}$ and extra peak intensity at $2.8\sigma_{11}$ that can be explained by the presence of hexagonal packing of large particles.

We used the positions of the first minima in the PPDFs as cutoff distances for defining nearest particle neighbours when calculating the local coordination environments and the various orientational order parameters. For reference, these are listed in Table C.16.
Structure Factors

The partial structure factors were calculated from the PPDFs as explained in Section 5.3.2. They are plotted along with the total structure factor in Figures 6.23 and C.8. We note that $S_{11}(k)$ has very weak structure, indicating the lack of a strong characteristic lengthscale for short-range ordering about the small particles. Also, the second peak in $S_{22}(k)$ does not show the splitting characteristic of crystalline domains of large particles (see discussion in Section 7.2.3), indicating the absence of such crystalline domains.

The first peaks in $S_{11}(k)$ and $S_{22}(k)$ are the most intense, and show very little

![Figure 6.23](image_url): The partial structure factors $S_{11}(k)$ and $S_{22}(k)$ for temperatures from $T = 5$ down to $T = 0.2$. For clarity, each curve below $T = 5$ has been shifted upwards by 0.2 units above the higher temperature curve directly preceding it.
variation with temperature. Their approximate positions are given by the wave vectors \( k_1 = 3.64\sigma_{11}^{-1} \) and \( k_2 = 5.5\sigma_{11}^{-1} \), respectively. We have used these wave vectors to calculate the incoherent scattering functions presented in Section 6.4.3.

**Local Structure**

Several quantities were used to characterise the local structure of the non-equimolar mixture. In Figure 6.24 we present the ‘bond’ fractions \( n_{ab} \), defined as the fraction of all nearest neighbours particle pairs that occur between particles of type \( a \) and \( b \) (see Table C.16 for nearest neighbour cutoff lengths). Upon cooling below \( T = 1 \), there is a small increase in \( n_{12} \) and an associated decrease in \( n_{11} \). However, the dominant interactions in the system are in roughly equal measure large-large and large-small, at all temperatures.

To investigate the local structure in more detail we consider the local environment about each particle. In Figure 6.25 the distribution of local packing environments is plotted as a function of temperature. There is no clearly dominant environment at low temperature. At \( T = 0.2 \), five environments make up 75% of the local structure, and a further four environments contribute a further 20%. Still, the structure appears

![Figure 6.24](image-url)

**Figure 6.24:** ‘Bond’ fractions as a function of temperature for \( T \leq 1 \). \( n_{ab} \) is the fraction of all nearest neighbours particle pairs that occur between particles of type \( a \) and \( b \). Error bars represent one standard deviation.
more homogenous, and the distribution of local environments is less diverse, than in the equimolar additive glass-former studied in Part I. For comparison, the latter has over 20 different local environments with none contributing more than 10% of the total.

There is little sign of H2 crystalline order in the system; below $T = 0.6$ the fraction of particles in S14 environments decreases sharply and less than 5% of large particles are in L43 environments. There is also little sign of crystallisation of the large particle fraction; the L06 environment, corresponding to a hexagonal cluster of large particles, shows only a small increase upon cooling and never constitutes more than 5.5% of large particle environments.

That said, there are some significant changes in local structure upon cooling. Below $T = 1$, the fractions of S05 and L34 environments rise dramatically and, intriguingly, become equal. Analysis of a configuration at $T = 0.2$ [Figure 6.20(c)] suggests that the reason for this is that the L34 environment is strongly associated
Figure 6.26: (a) Small particle environments in the low-temperature liquid, and (b)-(d) some common ways in which these pack together to form vertices about large particles. The filled and open circles indicate small and large particles, respectively. Note that the large particles at the centre of (b) and (d) both have $L_{34}$ local environments. Occasionally an H2 cell, consisting of two overlapping $S_{14}$ environments, replaces the square cell in structure (d).

with the packing of pentagonal $S_{05}$ units together with triangular units of three large particles and, occasionally, square $S_{04}$ units and pentagonal $S_{14}$ units. These local structural units are illustrated in Figure 6.26(a), and some of their more common packings are illustrated in Figure 6.26(b), (c) and (d). Observe that the large particles at the centre of (b) and (d) both have $L_{34}$ local environments. Occasionally an H2 cell, consisting of two overlapping $S_{14}$ environments, replaces the square cell in structure (d).

The preference for the $S_{05}$ environment over the $S_{14}$ environment is at first surprising. When all interparticle distances are set equal to $\sigma_{ab}$, the $S_{14}$ environment has an angle sum about the small particle of $363^\circ$. In contrast, the $S_{05}$ environment has an angle sum of $395^\circ$. We propose that the reason for this preference is that a higher proportion of $S_{14}$ environments would force an increase in the number of large-large particle contacts which, due to the non-additive interparticle potential, would result in an increase in the system volume. This hypothesis would also explain the very low number of small particles with more than one small neighbour and the absence of a larger increase in $L_{06}$ environments upon cooling. Glass-formation in this system may therefore be related to the idea of ‘frustration’, i.e. competition between optimal local and global packings.
Orientational Order Parameters

In order to quantify the orientational order in the system, we used the $n$-fold orientational order parameters, defined in Section 5.3.2. The bulk averaged $n$-fold order parameters $\Psi_n$ probe the local orientational order, and are plotted in Figure 6.27. The major change upon cooling is a large decrease in $\Psi_{6,1}$ below $T = 1$. This, together with a small decrease in $\Psi_{4,1}$, is consistent with the large increase observed in S05 environments which are expected to have roughly 5-fold local orientational

![Graph showing temperature dependence of $\Psi_n$]

**Figure 6.27:** The temperature dependence of the bulk averaged $n$-fold order parameters $\Psi_n$, where $n = 4, 6, 12$, and their small ($\Psi_{n,1}$) and large ($\Psi_{n,2}$) particle contributions. The error bars represent one standard deviation about the average.
order. $\Psi_{6,2}$ is quite high but shows only a small increase below $T = 1$. This, together with the large decrease in $\Psi_{6,1}$, indicates that there is no significant growth of a substitutionally disordered large-particle crystal phase.

We also tested for long-range orientational correlations between the local $n$-fold domains (defined in Section 5.3.2). We found no structure in $G_{4,2}(r)$ and only a single peak in $G_{6,1}(r)$ at all temperatures. Figure 6.28, shows the partial 4-fold orientational correlation function about small particles $G_{4,1}(r)$ and the partial 6-fold orientational correlation function about large particles $G_{6,2}(r)$. Some weak local correlations develop upon cooling, however there is clearly no long-range 4-fold orientational order in the system. There is also no sign of long-range 6-fold order in the system, but $G_{6,2}(r)$ develops structure out to $r = 6-8\sigma_{11}$ upon cooling, with a peak structure similar
to that observed in systems with substantial hexagonal crystalline domains of large particles (see, for example, Figure 7.9). Considering the lack of a substantial increase in $\Psi_{6,2}$ and in $L06$ environments upon cooling, this change must be mainly due to an increase in the orientational order within existing clusters of hexagonally-packed large particles.

We conclude that the non-equimolar mixture shows no sign of crystallisation or phase separation upon cooling from the liquid state. The low-temperature structure appears to be dominated by two types of medium-range order, small domains of hexagonally-packed large-particles, and larger domains of pentagonal $S05$ environments packed together with each other and with some $S04$ environments, H2 units and triangular packings of large particles. In the next section, we present an analysis of the changes in particle transport and structural relaxation that occur during cooling.

### 6.4.3 Supercooled Liquid Dynamics

**Intermediate Scattering Functions and Arrhenius Plot**

The timescale of structural relaxation can be probed quite readily by computing density correlation functions such as the intermediate scattering functions (see Section 5.3.3 for their definitions). Log-linear plots of the self intermediate scattering functions are shown in Figure 6.29, and have been measured at the positions of the first maxima in the static structure factors $S_{11}(k)$ and $S_{22}(k)$. The positions of these maxima are independent of temperature and are listed in the caption to Figure 6.29. The relaxation curves broaden with decreasing temperature until below $T = 0.45$ they are no longer able to decay to zero within the finite time scale of the simulations. The relaxation functions already span over five decades in time at this temperature. Below $T = 0.6$, a step appears in the relaxation curves at intermediate times. This step broadens into a plateau with an amplitude that increases with decreasing temperature. The height of the plateau also increases with decreasing temperature. Such two-step relaxation functions have been observed in a wide range of glass-forming systems as discussed in Section 1.2. Damped oscillations are also observed in the plateau region similar to what has been observed for the equimolar mixture with $\sigma_{12} = 1.2$ [44].
Figure 6.29: The incoherent scattering functions $F_{s,1}(k, t)$ and $F_{s,2}(k, t)$ for the small and large particles, respectively. The wave vectors $k_1 = 3.64\sigma_1^{-1}$ and $k_2 = 5.5\sigma_1^{-1}$ are the first peak positions in the respective partial structure factors. From left to right the temperatures of the curves are $T = 5, 3, 2, 1, 0.9, 0.8, 0.7, 0.65, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35, 0.3, and 0.2$. Note the appearance of a two-step relaxation process in the intermediate scattering functions.

Interestingly, $F_{s,2}(k, t)$ decays substantially faster than $F_{s,1}(k, t)$ at a given temperature. The height of the plateau in $F_{s,2}(k, t)$ is also substantially lower than the height of the plateau in $F_{s,1}(k, t)$ at the same temperature. This indicates that the large particles are able to relax their local structure faster than the small particles, which is rather unusual.

The temperature dependences of the structural relaxation times, plotted in Figure 6.30, appear to be Arrhenius at high temperatures, but diverge strongly from Arrhenius dependence as the temperature drops below $T = 0.65$. In contrast, the diffusion constants - measured in the region where the mean-squared displacement (MSD) has reached its long-time constant value ($R_a^2(t) > \sigma_{11}$) - show a weaker deviation from
Figure 6.30: Arrhenius plot of the structural relaxation times $\tau_{e,1}$ and $\tau_{e,2}$ and the inverse diffusion constants $D_1^{-1}$ and $D_2^{-1}$. The dashed lines are linear regressions through the data for $T \geq 0.65$. Note the divergence from Arrhenius behaviour at low temperatures.

Arrhenius temperature dependence, with the onset of this deviation occurring below $T = 0.6$. The diffusion constants for the small and large particle species remain approximately equal at all temperatures. The shorter structural relaxation times for the large particles, and the similar diffusion constants for the two species, suggest that although large particles are able to relax their local environments faster, the motion of both species becomes coupled at longer times and length scales.

For reference, the mean-squared displacements (MSDs) are plotted in Figure C.7, and the structural relaxation times and diffusion constants are listed in Table C.14. We note that the MSDs also show typical supercooled liquid behaviour.

The Non-Gaussian Parameters

The non-Gaussian parameters are plotted in Figure 6.31. A rapid rise in non-Gaussian behaviour is observed at low temperature for both the large and small particle species. The maximum values of the parameters increase rapidly below $T = 0.55$, with the peaks being slightly larger for the small particles. The trend is for the maxima to
Figure 6.31: The non-Gaussian parameter averaged over all particles, $A(t)$, and averaged over small and large particles, $A_1(t)$ and $A_2(t)$, respectively. The temperatures of the curves are as listed in Figure 6.29. Observe the rapid increase in the peak heights with decreasing temperature.
move to longer times as they increase in height. Below \( T = 0.4 \) the finite observation time of the simulations is too short to observe the maxima. \( A_2(t) \) and \( A_1(t) \) are no longer able to decay to zero for \( T < 0.45 \). From this, and the behaviour of the intermediate scattering functions and MSDs, we conclude that the system falls out of equilibrium somewhere near \( T = 0.45 \).

In summary, the non-equimolar mixture shows changes in dynamic behaviour upon cooling that are typical of fragile glass-forming liquids. This, together with the lack of any sign of crystallisation or development of long-range order in the liquid, lead us to conclude that this model is a good glass-former.

6.5 Discussion and Conclusions

The equimolar mixture forms a substitutionally ordered crystal phase when cooled at a constant pressure of \( P = 13.5 \). The crystal can be described as a tiling of the plane by a unit cell consisting of two small particles surrounded by six large particles in an elongated hexagonal arrangement. This H2 unit cell has been predicted to form one of the ground states for binary hard disc mixtures [155]. We find that the unit cells pack together both in parallel, and in a herringbone arrangement where the cells lie at approximately 80° to each other. From analysis of rearrangements in the growing crystal, it appears that the parallel arrangement is the more stable one. However, the herringbone arrangement is present in high concentration in the crystal nucleus and at the crystal-liquid interface and we therefore postulate that it is a kinetically preferred structure, and that it provides a kinetically preferred growth interface. The parallel arrangement has also been found to be one of the ground states for a 2D binary Lennard-Jones model studied in the context of quasicrystal stability [161]. This latter model, however, has significantly different interaction lengths to the present model and forms a wide variety of other structures that were not observed in the present system.

Heating of a crystal consisting of a perfect parallel packing of H2 cells revealed a hysteresis region in the isobaric phase diagram extending from \( T = 0.6 \) to \( T = 0.8 \). This is very large compared to the hysteresis regions observed for freezing/melting in the single-component soft-disc system at the same pressure, extending from \( T = 0.95–0.98 \), and for the S1 crystal phase studied in Chapter 5, extending from \( T = 1.02–1.06 \). When a defective crystal was heating from \( T = 0.6 \) we found that melting
6.5 Discussion and Conclusions

occurred at $T = 0.7$ but not at $T = 0.68$. The true thermodynamic melting/freezing temperature is therefore expected to lie somewhere between $T = 0.69$ and $T = 0.8$. We found that the low-temperature liquid exhibited dynamic behaviour typical of supercooled systems: the structural relaxation times and diffusion constants depart from an Arrhenius temperature dependence below $T = 0.7$, the maximum in the non-Gaussian function at intermediate times increases rapidly in magnitude at low temperature, and the intermediate scattering function has a clear step in the decay curve at $T = 0.6$. Below $T = 1$, the proportion of local crystalline environments in the liquid also rises rapidly, and at $T = 0.6$ over 50% of particles are in H2 cells. Yet, the supercooled liquid remains stable to crystallisation over timescales that are at least 2 orders of magnitude longer than the structural relaxation times and over which the average particle travels 3.5–10 diameters.

The high metastability of the supercooled liquid phase appears to be due to the slow process by which H2 cells align correctly for crystal growth to proceed. Although the majority of particles are in local H2 order at $T = 0.6$, these form only small clusters, on average 3–4 H2 units across, that remain unaligned with respect to each other. Only after more than 3,000 structural relaxation times ($\tau_{e,1}$) do a sufficient number of H2 cells align for the fraction of local crystalline environments to start increasing. Close-packing of H2 clusters in arrangements that cannot grow to fill space may be a reason for the slow rate of alignment of H2 cells. Crystal growth then appears to proceed via both aggregation events, involving the joining of several crystalline domains, and addition events involving the formation of new crystalline order in the liquid adjacent to the growing crystal. The initial crystal nucleus and the growing crystal contain a high proportion of herringbone packing of H2 cells, but the fraction of parallel packing appears to increase once the main growth event is complete, i.e. the crystal is quite labile to interconversion between different parallel and herringbone packings. Small distortions in the local coordination environment about small particles - from the S14 to S04 environment - may form a pathway for such interconversions to take place.

In contrast, the non-equimolar mixture shows little sign of H2 crystal order or phase separation into single component crystalline domains. The low-temperature structure is instead dominated by S05 environments and an equal number of L34 environments. The equal occurrence of these two environments appears to be due to the specific way in which the pentagonal S05 environments pack together with each
other and with occasional S14 and S04 environments. This system shows dynamic behaviour typical of other glass-forming liquids: the structural relaxation times and diffusion constants depart from an Arrhenius temperature dependence below $T = 0.6$, the maximum in the non-Gaussian function at intermediate times increases rapidly in magnitude around the same temperature, and the intermediate scattering function develops a clear two-step decay in the low-temperature liquid state. We therefore conclude that this model is a good glass-former. In contrast to the equimolar glass-former studied in Part I, this system has a more homogeneous structure and less diversity of local environments. It will therefore be interesting to compare the spatial distribution of dynamic heterogeneity in this system with that found for the structurally different glass-former in Part I.
Chapter 7

Nanocrystallinity and Phase Separation

In this chapter we present studies of two further soft-disc mixtures. The non-equimolar mixture with composition \( x_1 = 0.3164 \) of the additive system, i.e. with \( \sigma_{12} = 1.2 \), and the equimolar mixture of the non-additive system with \( \sigma_{12} = 1.3 \). We find that the former undergoes phase separation into an apparently stable crystal-amorphous composite, while the latter undergoes liquid-liquid phase separation before freezing of first the large-particle and then the small-particle fractions.

7.1 Introduction

As discussed in Section 4.2, amorphous alloys are of great technological interest because of their exceptional hardness, among other unusual properties. Pure metallic glasses, however, are also brittle, i.e. once they reach their elastic limit they fracture easily. To make them more suitable for a variety of applications, people have sought to improve their toughness by finding ways of forming crystalline domains that remain distributed within the amorphous matrix. Such nanocrystalline materials fall into the broader class of multiphase alloys [181,234] that include micro-segregated crystal-crystal composites such as the famous and beautiful Damascus steel swords [235,236].

The equimolar soft-disc mixture studied in Part I, with additive interparticle potential \( \sigma_{12} = (\sigma_{11} + \sigma_{22})/2 = 1.2 \), has previously been characterised as a good glass-former [44,67]. Here we study a non-equimolar mixture with composition \( x_1 = 0.3164 \) with the same set of interaction potentials, and find that, upon cooling, it undergoes
partial phase separation into a stable crystal-amorphous composite. This system may therefore be a useful model with which to increase our understanding of nanocrystalline materials, including both the relationship between their microscopic and mechanical properties and how to stabilise them.

We also study the phase behaviour of the equimolar mixture with interparticle potential $\sigma_{12} = 1.3$, which being greater than additive, results in an effective repulsion between unlike particle species. Not surprisingly, we find that this mixture undergoes liquid-liquid phase separation before freezing of first the large particle fraction and then the small particle fraction. In terms of interparticle potential, this places the glass-forming alloy studied in Part I between the competing extremes of phase separation, on the one hand, and formation of a substitutionally ordered crystal, on the other. The latter, of course, refers to the H2 crystal characterised in Chapter 6.

The rest of this chapter is structured as follows. In Section 7.2 we characterise the changes in structure and dynamics during cooling of the non-equimolar additive mixture, and in Section 7.3 we present a brief study of the phase behaviour of the equimolar mixture with $\sigma_{12} = 1.3$. This is followed by a short discussion and summary of the main results.

### 7.2 Crystal-Amorphous Coexistence in the Non-Equimolar Mixture with $\sigma_{12} = 1.2$

#### 7.2.1 Model and Computational Details

We consider a 2D system consisting of a binary mixture of particles interacting via purely repulsive potentials of the form

$$u_{ab}(r) = \epsilon \left( \frac{\sigma_{ab}}{r} \right)^{12}$$

(7.1)

where $\sigma_{12} = 1.2 \times \sigma_{11}$ and $\sigma_{22} = 1.4 \times \sigma_{11}$. All units quoted will be reduced so that $\sigma_{11} = \epsilon = m = 1.0$ where $m$ is the mass of both types of particle. Specifically, the reduced unit of time $\tau = \sigma_1 \sqrt{m/\epsilon}$. A total of $N = 1024$ particles were enclosed in a square box with periodic boundary conditions.

The molecular dynamics simulations were carried out at constant number of particles, pressure ($P = 13.5$) and temperature using the Nosé-Poincaré-Andersen (NPA)
algorithm developed by Laird et al. [83,84]. The equations of motion were integrated using a generalised leapfrog algorithm [84], and are provided for 2D simulations in Appendix A along with further details of the NPA algorithm. The time step employed was \(0.05\tau\) for \(T > 1\), and \(0.01\tau\) for \(T \leq 1\). For argon units of \(\eta = 120k_B\), \(m = 6.6 \times 10^{-23}g\) and \(\sigma_{11} = 3.4\text{Å}\), these time steps correspond to approximately 10 and 20 femtoseconds respectively.

A non-equimolar mixture consisting of \(N_1 = 324\) small particles and \(N_2 = 700\) large particles (giving a composition of \(x_1 = 0.3164\) to 4 d.p.) was studied at 16 different reduced temperatures from \(T = 5\) to \(T = 0.3\). The starting configuration of the run at \(T = 5\) was an equilibrated configuration at \(T = 5\) for the equimolar mixture described in Chapter 2 with the appropriate number of small particles changed to large particles. The starting configuration of each lower temperature equilibration run came from the final configuration of the preceding higher temperature run. At all temperatures the equilibration runs were taken out until steady state was achieved, i.e. until the average thermodynamic properties remained constant in time. The equilibration run times were longer than the times taken for all the dynamic correlation functions investigated to decay to zero for \(T \geq 0.7\), and were at least an order of magnitude longer than the structural relaxation times for \(T \geq 0.45 / T \geq 0.55\) for the small/large particles. Table C.18 (in Appendix C.5) lists the temperatures of each state studied as well as the equilibration and production times. The final configurations of the equilibration runs were used to start the production runs. The ‘masses’ of the Anderson piston and Nosé thermostat were \(Q_v = 0.0001\) and \(Q_s = 1000\), respectively, for all temperatures.

### 7.2.2 Thermodynamic Properties

The isobaric phase diagram is plotted in Figure 7.1. The density increases smoothly with cooling showing no sign of a first order phase transition, although there is perhaps a small change in slope between \(T = 0.5\) and \(T = 0.6\). The thermodynamic averages for the potential energy per particle \((U)\), energy per particle \((E)\), enthalpy per particle \((H)\), and number density per particle \((\rho)\) are listed for reference in Table C.18. An equation of state has previously been calculated for this system [67] using data obtained for the equimolar mixture. We have verified that this equation of state is consistent with the thermodynamic results obtained at the current composition.
Figure 7.1: Isobaric ($P = 13.5$) phase diagram. Error bars represent one standard deviation. Note that the density increases smoothly with cooling.

7.2.3 Growth of Crystalline Domains During Cooling

Particle Configurations

Several changes in structure occur as the system is cooled (representative particle configurations are shown in Figure 7.2). The initially homogeneous liquid (a) appears to separate into regions of hexagonally packed large particles and an amorphous phase consisting of both small and large particles but the separation is incomplete and the two phases remain intermixed. By $T = 0.55$ crystalline domains of large particles have formed (b), but do not appear to grow (c) despite the apparent high mobility of the intermixed amorphous phase. At $T = 0.3$ (d), the entire structure is rigid and the phases remain intermixed.
7.2 Crystal-Amorphous Coexistence

![Figure 7.2: Representative particle configurations at (a) $T = 1$, (b) $T = 0.55$ after 50,000$\tau$ equilibration, (c) $T = 0.55$ after 100,000$\tau$ equilibration, and (d) $T = 0.3$. The small and large particles are represented by filled and open circles respectively.](image)

**Pair Distribution Functions**

The pair distribution function (PDF) and the partial pair distribution functions (PPDFs) have been defined in Section 5.3.2. They are shown for the current system in Figures 7.3 and 7.4. Upon cooling, $g_{22}(r)$ develops structure over increasing lengthscales until by $T = 0.55$ there is still structure at $r = 10\sigma_{11}$, suggesting that there is some translational correlation between the large particle domains. There is no evidence of long-range translational order in the other PPDFs. The PDFs are also sensitive measures of local compositional correlations. For example, integrating
under the first peak of the distribution functions out to the first minimum provides
the partial coordination numbers, which are calculated in slightly different form in
Section 7.6. We extract the positions of the first minima in the PPDFs (listed in
Table C.19) to use as cutoff distances for defining nearest particle neighbours when
calculating the local coordination environments and the various orientational order
parameters.

Figure 7.3: The partial pair distribution functions $g_{11}(r)$ and $g_{22}(r)$ as a function of
distance from $T = 5$ down to $T = 0.3$. For $T \leq 3$, each curve has been shifted upwards by
one unit from the higher temperature curve directly preceding it. Note the different $x$-axis
scales.
Figure 7.4: The partial pair distribution function $g_{12}(r)$ and the total pair distribution function $g_{\text{all}}(r)$ as a function of distance from $T = 5$ down to $T = 0.3$. For $T \leq 3$, each curve has been shifted upwards by one unit from the higher temperature curve directly preceding it.

Structure Factors

The partial structure factors were calculated from the PPDFs as explained in Section 5.3.2. They are plotted along with the total structure factor in Figures 7.5 and C.10. The oscillations at small $k$ below the first maxima are artifacts of the Fourier transformation procedure (due to truncation of the PDFs at non-zero values) and should be ignored. For $S_{22}(k)$, the second peak is split into two components at all but the highest temperatures. The components of the bimodal second peak in $S_{22}(k)$ occur at wave vectors that coincide with the second and third peaks (at $k \approx 9.2\sigma_{11}^{-1}$ and $k \approx 10.5\sigma_{11}^{-1}$, respectively) in the static structure factor of a single component.
crystal of large particles. We conclude that this feature is due to the presence of crystalline domains of large particles at low temperatures.

Local Structure Parameters

Several quantities were used to characterise the local structure of the non-equimolar mixture. In Figure 7.6 we present the ‘bond’ fractions $n_{ab}$, defined as the fraction of all nearest neighbours particle pairs that occur between particles of type $a$ and $b$ (see Section 7.2.3 for the definition of nearest neighbours). Upon cooling below $T = 1$, $n_{12}$ decreases continuously from 0.4 until a new plateau value of 0.3 is reached. In contrast, the fraction of nearest neighbour contacts between like particles, given by $n_{11}$...
Figure 7.6: ‘Bond’ fractions as a function of temperature for $T \leq 1$. $n_{ab}$ is the fraction of all nearest neighbours particle pairs that occur between particles of type $a$ and $b$. Error bars represent one standard deviation.

and $n_{22}$, increases with cooling. This is a clear indication that the mixture undergoes phase separation as it is cooled. It does not, however, appear to be demixing into two single-component phases. $n_{12}$ never decreases below a value of 0.3 and, although large fluctuations are observed in the instantaneous ‘bond’ fractions between $T = 0.55–0.4$, we observe no systematic change during the extremely long production runs listed in Table C.18.

The distribution of local packing environments is plotted as a function of temperature in Figure 7.7. Only the most common environments are shown. From this data it is clear that the fraction of hexagonally packed large particles L06 increases dramatically below $T = 1$. At the same time the number of large particles with small particle neighbours decreases substantially (see L15, L24, L33 and L25). Both these results are consistent with the appearance of large particle domains at low temperature. The main change in the local environment around small particles is an increase in the number of small neighbours; S42 increases while S14 decreases. S60 also shows a small increase, but the fraction of small particles with six small neighbours remains quite small, i.e. the small particles do not substantially aggregate into a single-component phase.
Figure 7.7: The distribution of local packing environments as a function of temperature. We have identified a particular neighbourhood with the following notation: A small particle with \( m \) small neighbours and \( n \) large neighbours is designated as \( S_{mn} \) and the analogous large particle is indicated as \( L_{mn} \).

**Orientational Order Parameters**

In order to quantify the orientational order throughout the system we have introduced the \( n \)-fold orientational order parameters (see Section 5.3.2 for their definitions). The bulk averaged \( n \)-fold order parameters \( \Psi_n \), plotted in Figure 7.8, probe the local orientational order. The major change upon cooling is an increase in the hexagonal order about large particles \( \Psi_{6,2} \), especially between \( T = 0.65 \) and \( T = 0.55 \). In contrast, \( \Psi_{6,1} \) shows a smaller increase. What little 4-fold order was present at high temperatures decreases with cooling. The variation in 12-fold order can be explained by the presence of 6-fold order in the mixture.

We also tested for the presence of long-range orientational correlations between the local hexagonal domains. In Figure 7.9, we plot the partial 6-fold orientational correlation functions \( G_{6,1}(r) \) and \( G_{6,2}(r) \) over a range of temperatures. (These functions are defined in Section 5.3.2.) As the temperature is reduced, long-range orientational correlations develop between local hexagonal environments around large particles. This,
Figure 7.8: The temperature dependence of the bulk averaged $n$-fold order parameters $\Psi_n$, where $n = 4, 6, 12$, and their small ($\Psi_{n,1}$) and large ($\Psi_{n,2}$) particle contributions. The error bars represent one standard deviation about the average.
Figure 7.9: The partial 6-fold orientational correlation functions $G_{6,1}(r)$ and $G_{6,2}(r)$ for the small and large particles, respectively. For clarity, functions have been offset vertically by 0.4 units above the preceding curve. Note the different scales for the x-axes.

along with the local coordination analysis described above, provides clear evidence for the growth of extended crystalline clusters of large particles upon cooling. The presence of orientational correlation even at a distance of $r = 20\sigma_{11}$ (roughly half the system size) indicates that an extended crystalline domain of large particles spans the entire system for at least $T \leq 0.55$. In contrast, correlations between small-particle hexatic environments remain short-ranged over the entire temperature range studied. There is no orientational correlation between local 4-fold order in the system, and that the 12-fold orientational correlation functions mirror the trends observed in the 6-fold orientational correlation functions and therefore do not appear to contain any additional information. For this reason, we do not show these here.
7.2 Crystal-Amorphous Coexistence

7.2.4 Development of Heterogeneous Dynamics

We have already shown that the non-equimolar mixture undergoes partial phase separation into a crystalline large-particle phase and an amorphous two-component phase when it is cooled. In this section, we present an analysis of the changes in particle transport and structural relaxation that occur upon cooling.

Intermediate Scattering Functions and Arrhenius Plot

Log-linear plots of the self intermediate scattering functions are shown in Figure 7.10. $F_{s,1}(k,t)$ and $F_{s,2}(k,t)$ (defined in Section 5.3.3) have been measured at the positions of the first maxima in the static structure factors $S_{11}(k)$ and $S_{22}(k)$. The positions of these maxima are independent of temperature and are listed in the caption to Figure 7.10. The relaxation curves broaden with decreasing temperature until at $T = 0.5$ (for the large particles) and $T = 0.4$ (for the small particles) they are no longer able to decay to zero within the finite timescale of the simulations. The relaxation functions already span over five decades in time at these temperatures. At $T = 0.65$ (for the large particles) and $T = 0.55$ (for the small particles) a step appears in the relaxation curves at intermediate times. This step broadens into a plateau with an amplitude that increases with decreasing temperature. The height of the plateau also increases with decreasing temperature. Such two-step relaxation functions have been observed in a wide range of glass-forming systems as discussed in Section 1.2. Note that $F_{s,1}(k,t)$ decays substantially faster than $F_{s,2}(k,t)$.

Structural relaxation times $\tau_{e,1}$ and $\tau_{e,2}$ are defined as the time taken for the incoherent scattering functions $F_{s,1}(k,t)$ and $F_{s,2}(k,t)$, respectively, to decay to $1/e$ of their initial values. The temperature dependences of these relaxation times (shown in Figure 7.11) appear to be Arrhenius at high temperatures, but diverge strongly from Arrhenius dependence as the temperature drops below $T = 0.7$ and $T = 0.6$ for the large and small particles, respectively. The onset of non-Arrhenius temperature scaling occurs at the same temperature at which the step first appears in the relaxation curves. Diffusion constants were measured in the region where the mean-squared displacements (MSDs) have reached their long-time constant value ($R_\sigma^2(t) > \sigma_1^2$). They show a weaker deviation from Arrhenius temperature dependence than the structural relaxation times, with the onset of this deviation occurring around the same temperature. $D_1/D_2 \approx 1$ above $T = 1$, but increases steadily upon cooling below $T = 0.7$, i.e. the large particles move increasingly slow relative to the small
Figure 7.10: The incoherent scattering functions $F_{s,1}(k_1, t)$ and $F_{s,2}(k_2, t)$ for the small and large particles, respectively. The wave vectors $k_1 = 6.32\sigma_{11}^{-1}$ and $k_2 = 5.44\sigma_{11}^{-1}$ are the first peak positions in the respective partial structure factors. From left to right the temperatures of the curves are $T = 5, 3, 2, 1, 0.9, 0.8, 0.75, 0.7, 0.65, 0.6, 0.55, 0.5, 0.45, 0.4, 0.35$ and $0.3$. Note the appearance of a two-step relaxation process in the intermediate scattering functions.

particles. For reference, the MSDs over all particles $R^2(t)$, and averaged over the two particle species $R^2_2(t)$ and $R^2_1(t)$, are plotted in Figure C.11 and the structural relaxation times and diffusion constants are listed in Table C.20. It is interesting to note that both the diffusion constants and relaxation times show behaviour that is typical of glass-forming systems despite the appearance of crystalline domains of large particles and a significant amount of phase separation in the system.
7.2 Crystal-Amorphous Coexistence

Figure 7.11: Arrhenius plot of the structural relaxation times $\tau_{e,1}$ and $\tau_{e,2}$ and the inverse diffusion constants $D^{-1}_1$ and $D^{-1}_2$. The dashed lines are linear regressions through the data for $T \geq 0.7$. Note the divergence from Arrhenius behaviour at low temperatures.

Non-Gaussian Parameter

As explained in Section 5.3.3, the non-Gaussian parameters $A_a(t)$ can be used as a measure of the degree of dynamic heterogeneity in a sample. Large values at intermediate times can be attributed to a broad distribution of local mobilities. The non-Gaussian parameters for the present system are plotted in Figure 7.12. A rapid rise in non-Gaussian behaviour is observed at low temperature for both the large and small particle species. The maximum value of $A_2(t)$ increases rapidly below $T = 0.65$, while the maxima in $A_1(t)$ show a similar but smaller increase below $T = 0.55$. The trend is for the maxima to move to longer times as they increase in height; at the lowest temperatures the finite observation time of the simulations is too short to observe the maxima.

$A_2(t)$ and $A_1(t)$ are no longer able to decay to zero by $T = 0.65$ and $T = 0.45$, respectively. This suggests that the system falls out of equilibrium somewhere near $T = 0.65$. However, the average small and large particle is still able to travel $10\sigma_{11}$ within this observation time, indicating that much of the system is still highly mobile.
Figure 7.12: The non-Gaussian parameter averaged over all particles, $A(t)$, and averaged over small and large particles, $A_1(t)$ and $A_2(t)$, respectively. The temperatures of the curves are as listed in Figure 7.10. Observe the different $y$-axis scales and the rapid increase in the peak heights with decreasing temperature.
7.3 Phase Separation

There must therefore be a broad distribution of mobilities among the large particles. We conclude that this is due to the distribution of large particles between crystalline and amorphous domains. While the average mobility of the large particles is still high at $T = 0.65$, some large particles must have low mobility (presumably those in the crystalline domains) and some must have very high mobility (presumably those in the amorphous domains). At $T = 0.45$ the average MSD for a large particle during equilibration is still greater than $\sigma_{11}$, yet the system no longer appears to be segregating (see Figure 7.6). This suggests that the crystal-amorphous composite structure is stable to further phase separation.

The dynamic properties clearly show that the equilibration run times were sufficiently long for the non-Gaussian parameters to decay to 0.2 or less for $T \geq 0.7$, and at least an order of magnitude longer than the structural relaxation times for $T \geq 0.55$. We therefore conclude that the non-equimolar mixture is very stable to complete phase separation, despite the presence of crystalline domains of large particles that span the simulation cell. Below $T = 0.7$ the non-equimolar mixture displays dynamic properties typical of supercooled liquids including: non-Gaussian dynamics; the appearance of a plateau in the MSD and scattering functions at intermediate times; and strong non-Arrhenius temperature dependence of the structural relaxation times, and to a lesser extent of the diffusion constants. We conclude that this behaviour is due to glass-formation in the substantial amorphous fraction of the system. The stronger non-Gaussian dynamics of the large particles is likely due to their distribution between the less mobile crystalline domains and the more mobile amorphous regions. We discuss this system further in Section 7.4.

7.3 Phase Separation in the Equimolar Mixture with $\sigma_{12} = 1.3$

Only a minimal set of cooling runs were studied for this system in order to identify the nature of the liquid to solid phase transition. Upon cooling, the liquid segregates into small and large particle fractions before freezing, initially of the large particle phase, and then of the small particle phase at a lower temperature. The freezing temperatures of both phases are substantially reduced relative to the freezing temperatures of the respective single component systems.
7.3.1 Model and Computational Details

We consider a 2D system consisting of a binary mixture of particles interacting via purely repulsive potentials of the form

\[ u_{ab}(r) = \epsilon \left[ \frac{\sigma_{ab}}{r} \right]^{12} \]  

(7.2)

where \( \sigma_{12} = 1.3 \times \sigma_{11} \) and \( \sigma_{22} = 1.4 \times \sigma_{11} \). All units quoted have been reduced so that \( \sigma_{11} = \epsilon = m = 1.0 \) where \( m \) is the mass of both types of particle. Specifically, the reduced unit of time \( \tau = \sigma_1 \sqrt{m/\epsilon} \). An equimolar mixture of \( N = 1440 \) particles were enclosed in a square box with periodic boundary conditions. The molecular dynamics simulations were carried out at constant number of particles, pressure \((P = 13.5)\) and temperature using the Nosé-Poincaré-Andersen (NPA) algorithm as described in Appendix A. The ‘masses’ of the Anderson piston and Nosé thermostat were set to \( Q_v = 0.0002 \) and \( Q_s = 1000 \), respectively, at all temperatures.

The system was studied at 12 reduced temperatures: \( T = 5, 3, 2.5, 2, 1.8, 1.6, 1.4, 1.2, 1, 0.8, 0.6, \) and \( 0.4 \). The initial configuration at \( T = 5 \) was an equilibrated configuration at \( T = 5 \) for the equimolar system described in Chapter 6, i.e. with \( \sigma_{12} = 1.1 \). The starting configuration for each lower temperature run was the final configuration of the equilibration run at the preceding higher temperature. The length of the equilibration runs was 1000\( \tau \) for \( T \geq 2 \) and 2000\( \tau \) for \( T \leq 1 \). At all temperatures the equilibration runs were taken out until steady state was achieved, i.e. until the average thermodynamic properties remained constant in time. Except for at \( T = 1.8 \), this took less than one quarter of the total equilibration runtime. Densities were calculated using the latter part of the equilibration runs, i.e. after steady state had been achieved. No additional production runs were studied.

7.3.2 Changes in Configuration and Density

Representative configurations are plotted in Figure 7.13. At \( T = 3 \) [plot (a)] the liquid is more or less homogeneous, although small one-component domains are already present. By \( T = 2 \) [plot (b)] it is obvious that the liquid has begun to separate into separate small- and large-particle phases. The degree of phase separation gradually increases as the temperature is reduced until at \( T = 1.2 \) [plot (d)] the two phases are almost completely demixed. At this point the large-particle phase crystallises into a hexagonal lattice with some small particles imbedded, i.e. a substitutionally
Figure 7.13: Representative particle configurations at (a) $T = 3$, (b) $T = 2$, (c) $T = 1.6$, (d) $T = 1.2$, and (e) $T = 0.4$. The small and large particles are represented by filled and open circles respectively.
Figure 7.14: Isobaric ($P = 13.5$) phase diagram. The dashed vertical lines indicate approximate temperature ranges for the different structural regimes: (a) homogeneous liquid, (b) inhomogeneous liquid, (c) crystal-liquid coexistence, and (d) crystal-crystal coexistence. Errors bars represent one standard deviation.

disordered single-component crystal. The small particle phase remains fluid until $T = 0.4$ at which point it also freezes into a hexagonal lattice. Thus the liquid appears to demix before crystallisation, first of the large particle phase and then, at a lower temperature, of the small particle phase.

The different structural regimes are roughly indicated on the phase diagram shown in Figure 7.14. Within the different regions, the density variation can be well approximated by linear fits with different slopes. It is interesting to see that the freezing temperatures of the large- and small-particle liquid phases in this system ($T_{f,2} \approx 1.3$ and $T_{f,1} \approx 0.5$) are substantially reduced relative to the freezing temperatures obtained for the respectively one-component systems ($T_{f,2} = 1.7$ and $T_{f,1} = 0.95$) [67, 85, 171]. Some longer runs in the inhomogeneous liquid region would be useful in order to check whether further phase separation occurs given sufficient time for larger-scale compositional fluctuations to take place. This may affect $T_{f,2}$, but seems unlikely to affect $T_{f,1}$.
The non-equimolar mixture undergoes partial phase separation into a crystalline large-particle phase and an amorphous two-component phase when it is cooled. The dynamic properties clearly show that the equilibration run times are sufficiently long for the non-Gaussian parameters to decay less than 0.2 above $T = 0.65$, and are at least an order of magnitude longer than the structural relaxation times above $T = 0.5$. We therefore conclude that the non-equimolar mixture is very stable to complete phase separation, despite the presence of crystalline domains of large particles that span the simulation cell. Below $T = 0.7$ the non-equimolar mixture displays dynamic properties typical of supercooled liquids, including non-Gaussian dynamics, non-Arrhenius temperature dependence of the diffusion constants and structural relaxation times, and the appearance of a plateau in the mean squared displacement and incoherent scattering functions at intermediate times. We conclude that this behaviour is due to glass-formation in the substantial amorphous fraction in the system. The stronger non-Gaussian dynamics of the large particles is likely due to their distribution between less mobile crystalline domains and more mobile amorphous regions.

One possible reason for the stability of the non-equimolar mixture to phase separation is that the use of a square simulation cell artificially stabilises the mixed structure with respect to the phase separated structure. The amorphous phase may act as filler between the crystalline domains which have the wrong dimensions to join up across the periodic boundaries. If the phase separated system does not pack efficiently into a square cell with periodic boundary conditions then it may not form despite being the thermodynamically more stable structure. The possibility of this occurring will be increased if the free energy difference between the mixed and separated structures is very small. One way to test this hypothesis would be to use a simulation cell with independent variation of the $x$ and $y$ dimensions to allow for a better fit of the cell dimensions to the preferred dimensions of the phase separated system. This artificial stabilisation of the mixed phase should also be system size dependent, becoming weaker with increasing size. In any case, the absence of greater phase separation in the non-equimolar mixture suggests that the free energy difference between the mixed and separated structures is not great. It may therefore still be a useful model in which to study the formation and properties of nanocrystalline materials.

We note that the mixture with $x_1 = 0.75$ has previously been investigated [237].
Despite the presence of large crystalline domains of small particles, the large particle fraction does not appear to cluster substantially and remains in the form of extended chain-like structures that separate crystalline domains of small particles. Thus structurally, this mixture appears similar to the mixture studied in this chapter with $x_1 = 0.3164$, except that the role of large and small particles is reversed.

Upon cooling, the equimolar mixture with $\sigma_{12} = 1.3$ separates almost completely into two single-component liquid phases. In terms of interparticle potential, this places the glass-forming alloy studied in Part I between the competing extremes of phase separation, on the one hand, and formation of a substitutionally ordered crystal, on the other. The latter, of course, refers to the H2 crystal characterised in Chapter 6. The large particle fraction in the phase separated system freezes around $T = 1.3$, but the small particle fraction remains fluid until about $T = 0.5$. Therefore the freezing temperatures of both phases are substantially reduced relative to their one-component systems ($T_{f,2} = 1.7$ and $T_{f,1} = 0.95$) \cite{67, 85, 171}. 