A Structural Approach to Glassy Systems

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Abstract

In 1952 Sir Charles Frank popularised the idea that the stability of supercooled liquids arises from a tendency of the particles to cluster together into small structures that are geometrically incommensurate with crystallisation. In this thesis the local structural arrangement of particles within a number of systems is considered. A method called the topological cluster classification (TCC) is used to detect local structures of particles that are equivalent to the potential energy minimum clusters of 13 or fewer particles in isolation. The dynamics of different local structural arrangements within a bulk are considered by developing an algorithm to quantify the lifetimes that the structures persist within the system.

The first system considered is a model colloid-polymer mixture, where the colloids self-assemble into small clusters. The structures of the clusters that form are mapped out as a function of attraction and repulsion strength of the colloidal interactions, and the density of the system. In the case of six-particle clusters, the entropic contribution to the free-energy must be accounted for in order to correctly predict the structures that prevail. As the strength of the colloidal attractions is increased, ergodicity is broken and the clusters become kinetically trapped. The structures formed under these conditions are determined by the aggregation sequence of the colloids from the random initial configuration. The effect of long-ranged electrostatic repulsions between clusters on the intra-cluster structure is considered. As the repulsion strength and density increase it is possible for the intra-cluster structure to be perturbed by the presence of neighbouring clusters, demonstrating that it may not always be appropriate to consider each cluster as if it were an isolated system.

The structure at liquid-gas interfaces is considered with the TCC algorithm by measuring the fraction of particles participating within clusters as a function of distance from the interface. The participation ratios monotonically decrease in the interfacial region between the liquid and the gas. For interfaces with a high surface tension, the orientations of two types of elongated cluster are found to align near to the free surface and to oscillate with respect to the density fluctuations of the interfacial layers that propagate into the bulk liquid.

The clustering of particles in two model supercooled liquids is considered. The temperature behaviour of the participation fractions of particles in clusters and the dynamical persistence of clusters at low temperatures are measured. The domains of long-lived clusters in the supercooled regime are characterised and an association with spatial heterogeneities in the dynamics is demonstrated. Correlation lengths for the static structure and the dynamic heterogeneities are found to grow on cooling, however the manners in which the lengths grow are different. An inverse power law reference potential for one of these systems shows clustering that is significantly different to the full system with attractions, even though the viscous slowdown of the two models is the same. We propose avenues for further research to clarify the relationship between local structure and the glass transition.
For 奈津実
Acknowledgements

First and foremost I would like to thank my supervisors Paddy Royall and Jens Eggers for their support and guidance. Paddy suggested many ideas for problems to study and Jens’s enthusiasm and encouragement helped me along my way.

I enjoyed a number of placements in Hajime Tanaka’s group at the University of Tokyo during the course of this work. His interest in supercooled liquids shaped much of the work in chapters 6, 7 and 8. I am very grateful for the help I received and stimulating conversations I could enjoy with the members of the Tanaka laboratory.

In addition to thanking my supervisors, I would also like to acknowledge the important role that a number of others have played as this work was undertaken. Stephen Williams originally designed the Topological Cluster Classification system and I completed this work upon the considerable foundations that he had laid. Stephen helped in many other areas, in particular with the technical subtleties of computational physics. Experiments by Chris Klix and Ken-ichi Murata provided inspiration for the work in chapter 4. Maia Godonoga performed some of the simulation and analysis work that features in chapter 5. Mark Pond asked me to think about clusters and isomorphs, and this resulted in chapter 8.

I enjoyed a fruitful collaboration with Thomas Speck where we examined the statistics of local structures in trajectories of supercooled liquids. Although much of our work does not feature here, that study proved a great help for my understanding and interpretation of my own results on structure in supercooled liquids.

I am indebted to many of the scientists working in the fields of soft matter and glassy physics for helpful discussions during the course of my studies. These were either conducted in person at conferences and graduate schools, via email, or anomalously through the peer-review process. I am also grateful to my friends and peers at the University of Bristol for creating a friendly and welcoming environment to work in.

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Author’s Declaration

I declare that the work in this dissertation was carried out in accordance with the requirements of the University’s Regulations and Code of Practice for Research Degree Programmes and that it has not been submitted for any other academic award. Except where indicated by specific reference in the text, the work is the candidate’s own work. Work done in collaboration with, or with the assistance of, others, is indicated as such. Any views expressed in the dissertation are those of the author.

Signed: ..................................................

Date: ..........................
Previous Publications

Sections of this thesis have been published in the following papers:


Other sections have been submitted for publication:


In addition, the author contributed to a number of other publications while working towards this qualification:


“You should care about finding out what the answer is. You shouldn't care too much about which answer is right, or you end up making mistakes.”

Sean Carroll, 2012.
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List of Abbreviations

AO  Asakura-Oosawa.
BCC  body-centred cubic.
BD  Brownian dynamics.
BOO  bond orientational order.
CBTIM  cluster bond-type index method.
CCE  characteristic crystallographic element.
CNA  common neighbour analysis.
CRVT  Chacón-Reinaldo-Falagán-Velasco-Tarazona.
CS  cluster symbol.
DLVO  Derjaguin-Landau-Verwey-Overbeek.
FCC  face-centred cubic.
FIRE  fast inertial relaxation engine.
HCP  hexagonal close packed.
IPL  inverse power law.
IS  inherent structure.
ISF  self-intermediate scattering function.
KA  Kob-Andersen.
KWW  Kohlrausch-Williams-Watts.
LJ  Lennard-Jones.
LSCA  largest standard cluster analysis.
MC  Monte Carlo.
MCT  mode-coupling theory.
MD  molecular dynamics.
MPI  message parsing interface.
MSD  mean-square displacement.
NH  Nosé-Hoover.
NP  Nosé-Poincaré.
PBCs periodic boundary conditions.
PG  point group.
PMMA poly(methyl methacrylate).
RFOT random first order transition.
SC  simple cubic.
SI  International System of Units.
TCC topological cluster classification.
VFA Voronoi face analysis.
VFT Vogel-Fulcher-Tammann.
WCA Weeks-Chandler-Andersen.
## List of Symbols

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CHAPTER 1

Introduction

1.1. Identifying local structure and the Frank conjecture

In a seminal paper from 1952, Sir Charles Frank proposed that the atomic-level arrangements of atoms within a liquid determine how readily the liquid will freeze when it is supercooled [1]. He demonstrated his argument by citing an example based on the Lennard-Jones (LJ) liquid. The maximum binding energy for a thirteen LJ atoms in a cluster occurs when the atoms are arranged at the centre and vertices of a regular icosahedron. The icosahedral arrangement has a higher binding energy than other possible arrangements for the thirteen atoms, and specifically it is 8.4% higher in energy than arrangements from face-centred cubic (FCC) and hexagonal close packed (HCP) crystal lattices.

Using this energetic argument, Frank conjectured that the icosahedral arrangement of the atoms would be more prevalent within the supercooled liquid than the crystalline arrangements. The five-fold symmetries of regular icosahedra mean that they cannot fill a Euclidean volume without leaving gaps, hence crystallisation into a structure of repeating icosahedra does not occur. The five-fold symmetries of icosahedra are incommensurate with the six-fold symmetries of the FCC and HCP clusters, which do tile Euclidean space without gaps and are crystal phases for the LJ system. Frank therefore inferred that the presence of icosahedra within the supercooled liquid state would offer resistance to crystallisation, as the icosahedral structures of particles would have to rearrange in order for crystallisation to occur. He argued that this rearrangement would be costly in terms of energy in small localities and only become viable when extended over a large volume.

It turns out that this conjecture is falsifiable [2–4], however Frank’s work popularised the idea that local structuring of particles at a microscopic level can influence the state of a system and its dynamics on a macroscopic scale [5–9]. The idea that stable local structures of particles exist within supercooled liquids has been incorporated into a number
of theories for the glass transition [9–11], and a rationalisation for dynamic arrest in gels [12].

In order to ascertain the roles played by local structures of particles in a given system it is necessary to be able to identify their presence. There are a number of methods available to do this, and commonly used algorithms include Voronoi face analysis (VFA), common neighbour analysis (CNA) and bond orientational order (BOO) parameters [7, 13, 14]. In general these methods take the coordinates of the particles as an input to the algorithm for detecting local structures, which means they cannot readily be applied for atomic and molecular systems. For this reason studies of local structure have traditionally employed systems where the constituent particles are individually resolvable, such as computer simulations or experiments on colloids or grains. Some information on local structuring in atomic and molecular systems is accessible using advanced spectroscopic techniques, however.

In chapter 3 of this thesis we review a number of different methods for identifying local structure, and provide examples for systems where the methods have been applied. As mentioned, analysis of local structure has been a feature of many studies into supercooled liquids and gels. In addition to these two cases, there has been interest in the local arrangement of particles in equilibrium liquids [15], crystallising systems [13, 16], clusters [14] and interfaces [17].

In this thesis we employ a method known as the topological cluster classification (TCC) system to identify local structures of particles within bulk systems [18]. The method identifies clusters that are topologically equivalent to a set of reference clusters. In its original formulation the TCC algorithm identifies the ground state clusters of the Morse potential for thirteen or fewer particles.

In one respect the TCC algorithm can be considered as a method to test a generalised version of the Frank conjecture, for it identifies energy minimum clusters of a range of sizes from within bulk systems, rather than solely the thirteen particle case that was originally considered by Frank. In other respects it can be considered as a novel algorithm for detecting local structures based on the topology of the bonds between the particles. Detection routines can be designed and tailored for specific clusters in a system that are of interest in a system.

In this thesis we employ the TCC algorithm in both respects. We test the limits of the Frank conjecture by considering its applicability to clusters and supercooled liquids. We also employ the algorithm more generally as a tool to measure and identify any local structuring of particles in a variety of systems.

Full details of the TCC are given in chapter 3, where we define and develop detection routines for a wide range of clusters. We demonstrate the algorithm using simulations of LJ liquid and crystal phases.
Figure 1.1: Identification of local structures in a colloidal gel with the TCC algorithm. The particles are coloured depending on the size of the largest local structure that they are identified within. Image reproduced from reference [12].
Figure 1.2: Advances in particle synthesis techniques have yielded a wide variety of isotropic and anisotropic building blocks that can be used in self-assembling systems. Image reproduced from [19].

1.2. Self-assembly of colloidal clusters

Self-assembly is the autonomous organisation of components into structures due to the local interactions between the components, and without the direction of an external field [20]. Recently there has been a surge in interest in the self-assembly of colloidal and nanoscale components. This is attributable to advances in the synthesis for the building blocks that undergo self-assembly [19]. Figure 1.2 shows the variety and diversity of nanoscale and colloidal components that can now be synthesised.

In addition to advances in particle synthesis, there have also been significant advances in the design and tunability of the interactions between the components in self-assembling systems [21–23]. It is now possible to reversibly control the interactions between colloidal components, which allows self-assembly processes to be engineered and directed. In the long term it is expected that self-assembled structures will find novel applications in nanotechnologies and biotechnologies [19, 20].

In order to understand and design self-assembly processes, it is necessary to have a
handle on the energetic, thermodynamic and kinetic properties of the system [24, 25]. Theoretical and simulation work has an important role to play here, as often the relative simplicity of the interactions and the dynamics, and the relatively small number of components in self-assembling systems, mean that self-assembly problems are amenable to be tackled with theoretical and simulation techniques.

In chapter 4 we consider the self-assembly of spherical colloids into small clusters. Our simulation work is inspired by some experiments on colloidal dispersions where clusters are formed due to depletion interactions between the colloids (figure 1.3(a)) [27]. The aim of our work is to numerically map out state diagrams for the yield of different clusters that are formed by self-assembly. Parameters considered are the depletion attraction strength, the strength of any electrostatic repulsions between the colloids, and the density of the colloids within the system. The TCC algorithm is used to automate the process by which different types of cluster are identified.

The results of chapter 4 are pertinent to the energetics, thermodynamics and kinetics of the self-assembly process, and they inform us of the type of interactions that may need to be included in order to explain the experimental results. The dynamics of colloidal clusters once equilibrated are addressed in chapter 6. In chapter 6 a method is developed to measure the lifetimes of different structural states of the clusters, and to identify the transitions between the different states.
1.3. Structure at interfaces

The structure of liquids at an interface is an area of research with a long history. Raleigh and van der Waals first described the structure of a liquid-gas interface with a density profile that changes monotonically between the two phases in the late 19th century [28, 29]. More recently classical density functional theories for inhomogeneous fluids have been successful in describing the structure of the interface for a wide variety of phenomena and interfacial scenarios [30, 31].

One interesting property displayed under certain conditions is surface layering of the particles [30]. Surface layers are oscillations in density that propagate into the liquid from the interface. Surface layering is typically displayed in systems with high interfacial tension, such as liquids confined by a hard wall, a crystal or an external field.

The structure of a liquid in contact with a crystal has been demonstrated to display orientational dependency. In particular, local structures with five-fold symmetries have been identified lying parallel to the interface in experiments and in simulations [17, 32].

A related problem to liquids under confinement is that of the free interface, i.e. when a liquid is in contact with a vapour. Typically the interfacial tension of free interfaces is lower than that for interfaces under confinement, and surface layering is not seen. However metallic liquids can be cooled to low temperatures relative to the critical point, leading to large surface tensions and surface layering [33–37].

In chapter 5 we consider how the local arrangements of the particles near a free interface differ from the arrangements in the bulk liquid. We study two systems: a LJ liquid where the interface is characterised by a smooth density profile; and a model for sodium where interfacial layering is seen. The local arrangements of the particles are detected with the TCC algorithm, and we consider the structuring as a function of the distance from the interface and degree of undercooling relative to the critical point.

We also consider if there is any orientational dependence of the structural ordering near to the interface. We examine the orientations of two elongated structures near to the free interface, finding that the tension of the interface and the interfacial layering causes the structures to adopt specific orientations preferentially near to the interface.

1.4. Structure in supercooled liquids, and the glass transition

The nature of the glass transition has been described as one of the deepest and most interesting unsolved problems in solid state theory [40]. The lack of consensus amongst the scientific community over the solution to the problem has received attention in the wider press [41]. A number of well-written review articles and books tackle the physics of the glass transition [38, 42–47], however the essence of the problem is displayed in
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Figure 1.4: (a) An ‘Angell’ plot showing the increase in viscosities of strong and fragile supercooled liquids on approach to the glass transition. Figure adapted from [38]. (b) Dynamic heterogeneities in a colloidal supercooled liquid. The fast particles are depicted as large spheres and the slow particles small spheres. The red and blue colouring of the larger spheres highlights two large clusters of fast particles, while the green spheres are other fast particles. Image reproduced from [39].

the plot in figure 1.4(a). If a liquid can be cooled below its melting temperature without crystallising, its viscosity will increase. Eventually the viscosity becomes so large that it is impractical to perform experimental measurements on the sample as if it were a liquid. At this point, conventionally defined as when the viscosity reaches $\eta = 10^{13}$ poise, the supercooled liquid is said to form a glass. The temperature $T_g$ at which this transition occurs is termed the glass transition temperature.

Figure 1.4(a) shows the viscosity as a function of inverse temperature, normalised by the glass transition temperature for a range of supercooled liquids. The behaviour of the liquids broadly fall into two different categories. For ‘strong’ liquids the viscosity grows in an Arrhenius-like fashion as the glass transition is approached. A single functional form describes the temperature dependency of the viscosity, including within the equilibrium liquid temperature range. ‘Fragile’ liquids are somewhat different: the viscosity grows in an Arrhenius-like manner at high temperatures, however as the glass transition is approached the viscosity increases much more rapidly, and changes by many orders of magnitude for a small change in the temperature.

What could be the cause of the rapid increase in the viscosity of fragile glass formers as the glass transition is approached? It should be noted that the glass transition defined at $\eta = 10^{13}$ poise is a purely dynamical transition, where the viscosity and hence temperature at the transition is set by human rather than theoretical motives. Pair correlation functions for the atomic structure show little change on approaching $T_g$, and
nothing remarkable happens to any thermodynamic properties in the temperature range approaching the transition.

A plausible theoretical scenario for the glass transition is the mode-coupling theory (MCT), which predicts a non-zero critical temperature where the viscosity diverges [48]. The theory predicts that as the temperature is lowered the atoms become localised within a ‘cage’ of neighbouring particles. This slows down the dynamics of individual particles as they have to break through the cage of neighbours in order to relax the liquid structure. A non-linear feedback mechanism couples small changes in the static structure factor on cooling to the dynamical correlation function, leading to dynamical divergence. The shortcoming of the theory however is that the critical temperature predicted by the theory is usually much higher than the glass transition temperature that is observed. Moreover the dynamical singularity predicted by MCT is never actually observed in practice, i.e. the viscosity always stays finite up to the glass transition.

The putative MCT transition is a purely dynamical phenomenon where the liquid falls out of equilibrium on experimental timescales. A number of alternative explanations for the dramatic slowdown in the dynamics of fragile glass formers purport that there is a thermodynamic origin. Evidence to support these standpoints predominantly originate from an observation made by Walter Kauzmann in the 1940s [49], who noted that a linear extrapolation for the difference in entropy between a supercooled liquid and its crystal phase appears to vanish at a finite temperature below the glass transition temperature. The temperature at which the entropy difference vanishes is known as the Kauzmann temperature.

In a wide range of systems the Kauzmann temperature is observed to lie close to a temperature where the dynamics are predicted to diverge by a Vogel-Fulcher-Tammann (VFT) fit for the viscosity [43]. This indicates there may be a thermodynamic origin for the glass transition, with a thermodynamic transition lying at a lower temperature than the glass transition temperature. This led to the development of Adam and Gibbs scenario for the glass transition, where the viscosity is an exponential function of the temperature and the difference in entropy between the supercooled liquid and the crystal not attributable to vibrational degrees of freedom [50].

A recent development that has had a major influence on the direction of the field is the discovery of spatial heterogeneities in the dynamics of supercooled liquids, or simply ‘dynamic heterogeneities’ [51–53]. On cooling the relaxation of atoms in a supercooled liquid become correlated in space. Regions of the liquid where the particles tend to either all be mobile or all be immobile over a certain timescale develop and grow in spatial extent as the glass transition is approached. This scenario is depicted in figure 1.4(b), where a number of particles relaxing in cooperative fashion are clustered together. The dynamic heterogeneities indicate that there is a growing dynamic lengthscale associated
with the glass transition, which can be construed as further evidence that a thermodynamic transition might be at play. The strength of this standpoint would be improved if it could be shown that there is a growing static correlation length on approaching the glass transition as well.

So what of the relationship between structure and the glass transition? Strong evidence that structure plays a role in the glass transition comes from studies in the isoconfigurational ensemble [54, 55]. This ensemble examines the trajectories that emerge from an initial supercooled liquid configuration where the particles are fixed but the velocities are randomly drawn from a Maxwell-Boltzmann distribution. The results of simulations in the isoconfigurational ensemble demonstrate that certain regions of the initial configuration have a higher propensity to relax before other regions, indicating that information about the correlated relaxation dynamics of the atoms is encoded within the configurations.

There are a number of theories for the glass transition which pertain that local arrangements of the atoms with identifiable structure are integral to the dynamic slowdown of fragile glass formers. The frustrated limited domains theory of the glass transition states that there are locally preferred structures of atoms in the liquid that differ geometrically from the local structures of the crystal [9]. In the absence of frustration, the liquid would freeze into the locally preferred structures at a second order thermodynamic critical point. However the presence of frustration set by the geometry of the space, cf. how icosahedra cannot crystallise in Euclidean space without incorporating defects, means that the transition is avoided. The theory predicts a zero temperature divergence for the viscosity and a growing correlation length for the size of the frustration limited domains on cooling.

An alternative standpoint has been advanced by Hajime Tanaka with the medium range crystalline order interpretation for the glass transition [11]. In this theory critical-like fluctuations of static crystalline order develop on cooling, and an associated correlation length for these domains grows in a one-to-one fashion with the dynamic correlation length. Bulk crystallisation of the system is frustrated by the presence of geometrically incompatible local structures in between the regions of high crystallinity. The static and dynamic correlation lengths, and the viscosity are predicted to diverge at a finite temperature ideal glass transition, with the viscosity obeying a VFT form.

Another theoretical framework for the glass transition considers the temperature behaviour of quasi-species, which can be interpreted as local arrangements of the atoms within the liquid [10]. A discrete statistical mechanics is defined from the concentrations of ‘liquid-like’ quasi-species, which decrease as the temperature is lowered. A static correlation length is defined from the average distance between liquid-like quasi-species, and is predicted to tend to infinity as the temperature approaches zero. The relaxation
time diverges only at zero temperature, i.e. there is no thermodynamic transition.

It is clear therefore that there a number of different theoretical approaches for the glass transition that relate the local structural arrangement of the atoms or particles within supercooled liquids to the anomalous dynamical behaviour. In this thesis we employ the TCC algorithm to elucidate the relationship between local structures of particles within a liquid and the glass transition. In particular we concern ourselves with the type and persistence (or stability) of local structures in supercooled liquids, and how local structures and dynamic heterogeneities are related.

In chapter 6 we consider how the lifetime of a particular local structural arrangement identified by the TCC can be defined and measured. From the distribution of lifetimes of different instances of a particular local structure, we are able to characterise the dynamics and stability of different types of local structure. In chapter 7 we study two model glass-forming models. The techniques developed in chapter 6 allow stable local structures to be identified from a single state point for each of the systems. The characteristics of the domains of particles participating in local structures are studied. Finally the temperature behaviour of static correlation lengths relating to the domains of structured particles, and the growing correlation length for the dynamic heterogeneities, are studied.

In chapter 8 the relationship between local structure in two supercooled liquids with similar relaxation dynamics is examined. One liquid is a LJ system with attractions between the particles, while the other is an inverse power law (IPL) reference system. The two systems are related by virtue of the fact that the LJ system with attractions displays strong correlations between the fluctuations of the potential and the virial in the canonical ensemble [56]. The consequence of this property is that the IPL reference system is a good match for the two-body structural and dynamical properties of the LJ system. Our study concerns the difference in local structure between the two liquids, and the consequences of this for theories of the glass transition pertaining to the importance of local structure.

Although the latter half of this thesis is concerned with local structure and the glass transition, we highlight two other popular theories for the transition that do not explicitly link local structures with glassy dynamics. The dynamical facilitation theory of the glass transition argues that the transition is a purely dynamical phenomenon associated with microscopic pathways by which particles relax, and that the liquid falls out of equilibrium on experimental timescales [57]. It predicts a growth in the viscosity to infinity only at zero Kelvin, and does not invoke any kind of thermodynamic transition to explain the glassy behaviour. A feature of the theory is a first-order dynamical phase transition that exists in an ensemble of trajectories. Recently it has been shown that the first-order trajectory-space transition can be induced by biasing the time-integral of a (TCC) structural order parameter, however the transition disappears as the trajectory length tends
to zero (i.e. configuration space) \[58]\).

The random first order transition (RFOT) theory of glasses predicts an ideal glass transition at the Kauzmann temperature and a VFT form for the increase in viscosity \[59]\]. As the temperature approaches the ideal glass transition temperature, the system breaks up into domains of long-lived aperiodic structures which grow in size on cooling. The origins of the theory lie in the physics of spin glasses, allowing us to highlight one of the wider benefits of research into the glass transition.

Work by Mézard et al. has transferred theoretical techniques developed for spin glass problems to the fields of computational complexity, optimisation theory, neural networks, image processing and message parsing \[60]\]. Their work demonstrates that glassy behaviour and glass transitions exist not only in the physics of spin glasses, but also in other branches of science. The long-term benefits of research into the atomistic glass transition may therefore be found in other systems that display features such as a dramatic dynamic slowdown or cooperative dynamics. Thus research into the atomistic glass transition is a worthwhile pursuit not only for the progress of this field, but also for the wider science of complex systems.

1.5. Overview of the thesis

Chapter 2 is a methods chapter where the details of the simulation techniques are given. Chapter 3 features a review of a number of different methods used to identify local structure in bulk phases, before proceeding to define the TCC algorithm and the clusters that it identifies. Chapter 4 is the study of the self-assembly of colloidal clusters and chapter 5 is the investigation into structure at liquid-vapour interfaces. In chapter 6 methods for studying the dynamics of the clusters from chapter 4 and in supercooled liquids are developed. Chapter 7 contains a study of the local structuring in two model supercooled liquids and the relationship with dynamic heterogeneities. In chapter 8 the behaviour of higher-order measures for structure and dynamics along isomorphic curves is considered, and a comparison is made between the structure and dynamics in a supercooled liquid with attractions and a purely repulsive IPL reference system. Chapter 9 states our conclusions and suggestions for future work.
1.6. Bibliography


Chapter 1. Introduction


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CHAPTER 2

Methodology and Simulation Details

2.1. Introduction

This chapter details the methodology of computer simulations, as used to study physical problems in this thesis.

Computer simulations are used to generate microscopic data on the state of a system of interacting particles (section 2.2). The particles may be atoms or colloids, for example, and the microscopic data are their positions and velocities. It is the province of statistical mechanics to link the microscopic data of individual configurations to macroscopic thermodynamic variables for the system, such as the energy, temperature and entropy.

An overview of the statistical mechanics concepts that are used in this thesis is given in section 2.3. A more complete description of this field is available in one of many textbooks on statistical mechanics [1–4, for example]. Definitions are given here for the concepts that underlie the simulation techniques that are employed in our studies.

Three types of simulation methods are employed depending on the physical system under study and the type of data required. These methods are namely molecular dynamics (MD), Monte Carlo (MC) and Brownian dynamics (BD), and they are described in section 2.4. The method deployed for a particular problem will depend on the physical nature of the system under study, the type of data that are required for analysis, and the timescales over which data are needed.

In order to simulate a physical system it is necessary to have a model for the particles and their interactions. All the systems studied in this thesis consist of free particles interacting via spherically symmetric pair-wise potentials. The potentials used are defined in section 2.5.

The final section contains technical details for the simulations (section 2.6). These details are the geometry under which simulations are performed, information about how initial configurations are prepared and equilibrated, and the reduced units that the simulations are performed in and the results are presented in terms of.
2.2. A system of interacting particles

Throughout this thesis physical systems such as colloidal dispersions (chapter 4), liquid-vapour interfaces in atomic systems (chapter 5), and supercooled binary metallic liquids (chapters 6, 7 and 8) are simulated with classical models. The model for the physical situation is called the system and its constituent species are the particles. In this section the nomenclature and symbols used to describe a system are given.

Each system is isolated and consists of $N$ classically interacting particles in three-dimensions with masses $m_1,\ldots,m_N$ in a volume $V$. The vector $\mathbf{r}$ denotes any position in the system relative to some fixed origin $0$. The instantaneous configuration, or microstate, of the system is defined by all the particle positions $\mathbf{r}^N \equiv \mathbf{r}_1,\ldots,\mathbf{r}_N$ and momenta $\mathbf{p}^N \equiv \mathbf{p}_1,\ldots,\mathbf{p}_N$. The number density of the system is $\rho = N/V$.

In the absence of any external field acting on the particles, the Hamiltonian is the total energy of the system:

$$H(\mathbf{r}^N, \mathbf{p}^N) = K_N(\mathbf{p}^N) + V_N(\mathbf{r}^N),$$ (2.1)

where $V_N(\mathbf{r}^N)$ is the total inter-particle potential energy and

$$K_N(\mathbf{p}^N) = \sum_{i=1}^{N} \frac{|\mathbf{p}_i|^2}{2m_i},$$ (2.2)

is the kinetic energy due to the motion of the particles.

The coordinates evolve in time $t$ obeying Hamilton’s equations of motion

$$\dot{\mathbf{r}}_i = \frac{\partial H}{\partial \mathbf{p}_i}, \quad \dot{\mathbf{p}}_i = -\frac{\partial H}{\partial \mathbf{r}_i} = \mathbf{F}_i,$$ (2.3)

where dots over the variables indicate time derivatives. The vector $\mathbf{F}_i$ is the total force acting on particle $i$ due to its interactions with the other particles. Given an initial configuration $\mathbf{r}_0^N, \mathbf{p}_0^N$, there is a deterministic solution of these equations. The solution is a time-dependent trajectory $\mathbf{r}^N(t), \mathbf{p}^N(t)$ through the $6N$-dimensional phase space.

2.2.1. Time averages

Certain thermodynamic properties of the system, known as the ‘mechanical’ properties, can be calculated as the averages of functions of the positions and momenta of the particles. These thermodynamic properties include the temperature, internal energy and pressure. However, macroscopic ‘thermal’ properties such as the entropy and free energy of the system cannot be calculated in this way.

The time average of an observable quantity $B$ that depends on the instantaneous con-
Chapter 2. Methodology and Simulation Details

The configuration of the system is

$$\langle B \rangle_t = \lim_{\tau \to +\infty} \frac{1}{\tau} \int_0^\tau B[r^N(t), p^N(t)] \, dt.$$  \hfill (2.4)

The subscript on the angular brackets is used to denote a time average.

The thermodynamic internal energy $U$ is the time average of the Hamiltonian energy

$$U \equiv \langle \mathcal{H} \rangle_t = \lim_{\tau \to +\infty} \frac{1}{\tau} \int_0^\tau \mathcal{H}[r^N(t), p^N(t)] \, dt,$$  \hfill (2.5)

and the temperature $T$ is given by the time average of the total kinetic energy

$$T \equiv \frac{2}{3Nk_B} \langle K_N(p^N) \rangle_t,$$  \hfill (2.6)

where $k_B$ is the Boltzmann constant.

The virial function $W$, given by

$$W(r^N) = \frac{1}{3} \sum_{i=1}^N r_i \cdot F_i,$$  \hfill (2.7)

provides a means to calculate the pressure $P$ via a time average via the virial equation:

$$PV = Nk_B T + \langle W \rangle_t.$$  \hfill (2.8)

2.3. An overview of statistical mechanics

Statistical mechanics provides a microscopic basis for thermodynamics by connecting the states and motions of the particles to the macroscopically observable variables such as the energy, temperature, pressure, entropy, free energy and heat capacity.

For a typical macroscopic system the number of particles is of the order $\sim O(10^{23})$. The amount of information needed to completely specify a microscopic configuration, using $r^N$, $p^N$ as discussed in section 2.2, is impractically large for systems of this size.

The premise of statistical mechanics is that the microscopic details of the system are largely unimportant in determining the macroscopic properties. This is because, when considering a system where its trajectories are derived from the same Hamiltonian, i.e. interacting with the same microscopic forces, a large number of the trajectories may display identical macroscopic quantities even if following different paths through phase space.

When considering the large number of trajectories that the system could take, it is useful to introduce the concept of the statistical ensemble. A statistical ensemble is a large collection of replicas of a physical system that share one or more macroscopic parameters
but are characterised by different microstates.

In statistical mechanics, thermodynamic quantities are calculated as the average values of observables across the different microstates in a statistical ensemble. It is assumed that these average quantities depend only on the distribution of values of the observable across the microstates and the probabilities that a system is in a particular microstate of the ensemble. Therefore statistical mechanics employs tools from probability theory to study the thermodynamic properties of systems containing large numbers of microscopic entities (e.g. atoms, molecules).

2.3.1. Ensemble averages

Returning to the observable \( B(r^N, p^N) \), its ensemble average\(^1\) depends on the weights that the different microstates of the system contribute to the phase space explored by the statistical ensemble. Letting the un-normalized weights of each microstate be given by \( w_e(r^N, p^N) \), the ensemble average of \( B \) is

\[
\langle B \rangle_e = \frac{\int \int B(r^N, p^N) w_e(r^N, p^N) dr^N dp^N}{\int \int w_e(r^N, p^N) dr^N dp^N},
\]

where the subscript ‘e’ is used to denote an ensemble average.

The denominator in equation 2.9 is known as the partition function for the ensemble and is written \( Q_e \). It provides the connection to thermodynamics by defining a thermodynamic potential \( \Psi_e \):

\[
\Psi_e = -\ln Q_e.
\]

The value of the potential \( \Psi_e \) takes its minimum value when the system is in its equilibrium thermodynamic state.

All thermodynamic observables of a system can be written in terms of relationships involving \( Q_e \) or its thermodynamic potential \( \Psi_e \).

Our simulations are performed in three different statistical ensembles, namely the microcanonical \( NVE \), canonical \( NVT \) and isobaric-isothermal \( NPT \) ensembles.

2.3.2. Ergodicity

A system is said to be ergodic if the time average of an observable coincides with the ensemble average, i.e.

\[
\langle B \rangle_e = \langle B \rangle_t.
\]

\(^1\) Defined only at thermodynamic equilibrium.
equilibration of samples and representative sampling of phase space.

From here on the subscripts \( t \) and \( e \) on the angular brackets are omitted. The notation \( \langle B \rangle \) is used to denote the equilibrium average of \( B \). In practice this average value is calculated from simulation data by either calculating time averages of single trajectories, or by averaging \( B \) of an ‘ensemble’ of statistically independent configurations derived from multiple simulations, or by a combination of the two methods.

### 2.3.3. The microcanonical ensemble

States of an isolated system are in the microcanonical \( NVE \) ensemble if they cannot exchange matter, energy or space with the rest of the universe. This means that the thermodynamic quantities of system size \( N \), volume \( V \) and energy \( E \) are constants for all the microstates in this ensemble.

The \textit{a priori} assumption of statistical mechanics is that each of the microstates of isolated systems are equally probable. Therefore, the classical partition function is just the continuous sum of all these states:

\[
Q_{NVE} = \frac{E_0}{h^{3N} N!} \int \int \delta(H(r^N, p^N) - E) \, dr^N \, dp^N ,
\]

where \( h \) is the Planck constant and the energy constant \( E_0 \) is needed in order that \( Q_{NVE} \) is dimensionless. The factor \( N! \) is required so that the number of microstates is not over-counted as the particles are not distinguished between. The \( \delta \) term is the Dirac delta function which selects only the microstates with the correct energy \( E \). The definition of \( \delta \) constrains it to satisfy the integral:

\[
\int_{-\infty}^{\infty} \delta(x) \, dx = 1 ,
\]

and that the following relationship for an arbitrary function \( f(x) \) also holds:

\[
\int_{-\infty}^{\infty} f(x) \delta(x) \, dx = f(0) .
\]

The microcanonical partition function is directly related to a thermodynamic quantity known as entropy \( S \) by

\[
-S = -k_B \ln Q_{NVE} .
\]

The entropy takes its maximum value when the system is in thermodynamic equilibrium.

Various thermodynamic variables can be written as a function of \( S \) (and consequently \( Q_{NVE} \), with

\[
\frac{1}{T} = \left( \frac{\partial S}{\partial E} \right)_{N,V} , \quad \frac{P}{T} = \left( \frac{\partial S}{\partial V} \right)_{N,E} .
\]
2.3.4. The canonical ensemble

In the canonical $NVT$-ensemble the system is in thermal equilibrium with a very large heat bath at temperature $T$. The heat bath fixes the temperature of the system at $T$, and the number of particles $N$ and the volume $V$ are other constant variables.

The partition function is

$$Q_{NVT} = \frac{1}{h^{3N}N!}\int\int\exp(-\beta\mathcal{H}(r^N,p^N))\,dr^N\,dp^N,$$  \hspace{1cm} (2.17)

where $\exp(-\beta\mathcal{H}(r^N,p^N))$ is the famous Boltzmann factor that gives the statistical weights for the microstates with energy $E = \mathcal{H}(r^N,p^N)$. The quantity $\beta$ is known as the thermodynamic beta and is defined as

$$\beta = \frac{1}{k_B T}.$$  \hspace{1cm} (2.18)

The associated thermodynamic potential is known as the Helmholtz free energy and is given by

$$F = -k_B T \ln Q_{NVT}.$$  \hspace{1cm} (2.19)

The entropy and pressure are related to $F$ by

$$S = -\left(\frac{\partial F}{\partial T}\right)_{N,V}, \quad P = -\left(\frac{\partial F}{\partial V}\right)_{N,T}.$$  \hspace{1cm} (2.20)

2.3.5. The isobaric-isothermal ensemble

The final statistical ensemble considered is the isobaric-isothermal $NPT$-ensemble, where both the pressure and the temperature of the system are fixed. The thermodynamic constants are therefore the number of particles $N$, the pressure $P$ and the temperature $T$.

The partition function is

$$Q_{NPT} = \frac{1}{h^{3N}N!V_0}\int\int\int\exp(-\beta(\mathcal{H}(r^N,p^N) + PV))\,dr^N\,dp^N\,dV,$$  \hspace{1cm} (2.21)

where $V_0$ is a constant with the units of volume that ensures $Q_{NPT}$ is dimensionless. The exponential factor gives the statistical weights for the microstates with energy given by the Hamiltonian $\mathcal{H}(r^N,p^N)$ and occupying a volume $V$ under the influence of the fixed pressure $P$.

The partition function in the isobaric-isothermal ensemble is related to the thermodynamic potential $G$, known as the Gibbs free energy, by the relation

$$G = -k_B T \ln Q_{NPT}.$$  \hspace{1cm} (2.22)
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The entropy and volume are given by the following functions of $G$:

\[ S = -\left(\frac{\partial G}{\partial T}\right)_{N,P}, \quad V = \left(\frac{\partial G}{\partial P}\right)_{N,T}. \]  

(2.23)

2.4. Simulation techniques

Computer simulations are used to generate microscopic-level data for the behaviour of particles in physical systems. Three different simulation methods are employed in this thesis, namely the MD, MC, and BD methods. The following sections contain details for how these methods are executed.

Readers who are looking for more details on the simulation techniques are directed to the excellent book on computer simulations by Allen and Tildesley [5], as well as references [6–8].

2.4.1. Molecular dynamics

The molecular dynamics (MD) method was pioneered by Alder and Wainwright to study the phase transition of the hard sphere system [9]. The method works by numerically integrating Hamilton’s equations of motion for the particles (equations 2.3). This yields a time-dependent trajectory through the phase space $(r_N(t), p_N(t))$ that is an approximation for the true trajectory of the system. In practice the trajectory generated by a MD simulation quickly diverges from the true trajectory of the system due to the chaotic nature of the Hamilton equations [10]. This said, proper MD simulations do in fact yield representative configurations for statistical ensembles\(^2\). It is also the case that the dynamics of MD trajectories are representative of the true dynamics of the system - at least on short time-scales.

Numerical integration schemes for MD simulations solve the equations of motion for discrete points in time. The positions and momenta are advanced from a configuration at time $t$, $(r_N(t), p_N(t))$, to a new configuration at a later time: $(r_N(t + \Delta t), p_N(t + \Delta t))$. The time increment $\Delta t$ is known as the simulation timestep. The timestep needs to be smaller than the fastest vibrational time of the system to ensure numerical stability of the integration. A choice of small $\Delta t$ needs to balanced against the requirements for the total simulation length and the computation time needed to complete the calculation.

\(^2\)Here “proper” MD simulations requires that: (i) the simulations are well equilibrated, i.e. time averages do not change along the trajectory and that the trajectory is not stuck in a statistically unrepresentative region of the phase space, and (ii) that the MD timestep is small enough that the macroscopic thermodynamic variables do not drift. Conditions for equilibration are discussed in section 2.6.6.
Molecular dynamics in the \( NVE \)-ensemble

To simulate a system in the microcanonical ensemble, equations 2.3 are integrated using the velocity Verlet method [11, 12]:

\[
\begin{align*}
\mathbf{p}_i(t + \frac{1}{2}\Delta t) &= \mathbf{p}_i(t) + \frac{1}{2}\Delta t\mathbf{F}_i(t), \\
\mathbf{r}_i(t + \Delta t) &= \mathbf{r}_i(t) + \Delta t\frac{\mathbf{p}_i(t + \frac{1}{2}\Delta t)}{m_i}, \\
\mathbf{p}_i(t + \Delta t) &= \mathbf{p}_i(t + \frac{1}{2}\Delta t) + \frac{1}{2}\Delta t\mathbf{F}_i(t + \Delta t).
\end{align*}
\] (2.24, 2.25, 2.26)

The velocity Verlet algorithm has a number of technical advantages that make it highly suitable for simulating systems in the \( NVE \)-ensemble. Firstly, it is known as a symplectic algorithm, as a Hamiltonian \( \hat{H} \) is strictly conserved along the simulation. The Hamiltonian \( \hat{H} \) is a perturbation of the true Hamiltonian \( H \) for the system. This means that the numerical estimate for the Hamiltonian, obtained from a velocity Verlet MD simulation, is always within a time-independent bound of the true Hamiltonian \( H \).

Secondly, the velocity Verlet method is a time reversible algorithm. This means that integrating any number of timesteps forwards in time from an initial configuration \((\mathbf{r}^N(0), \mathbf{p}^N(0))\), and then integrating the same number of steps backwards in time reproduces the same initial configuration (to within computational round off errors). These two properties ensure that numerical stability is achieved in long MD simulations when using double-precision floating-point arithmetic.

For systems where no external force acts on the particles, equations 2.26 conserve the total linear momentum of the system \( \mathbf{P} = \sum_{i=1}^{N} \mathbf{p}_i \). Therefore MD simulations only probe configurations from a subset of the microcanonical ensemble - namely the constant-\( NVEP \) ensemble.

Conserving \( \mathbf{P} \) adds three constraints to the particles momenta. These constraints must be considered when calculating properties of the system that depend on the number of degrees of freedom for the momenta. Temperature is an example of such a quantity, and the denominator in equation 2.6 changes to compensate for the reduction in the number of degrees of freedom for the momenta from \( 3N \) to \( 3N - 3 \) [13]:

\[
T = \frac{2}{3(N-1)k_B}\langle K_N(\mathbf{p}^N) \rangle.
\] (2.27)

Molecular dynamics in the \( NVT \)-ensemble

Two different MD schemes are used to sample states from the canonical ensemble. These schemes are both based on the extended phase space method of Nosé, which enables deterministic MD simulations at constant temperature to be performed [14, 15]. The effect of the Nosé constant temperature MD methods is to couple the system to a large
heat bath with fixed temperature.

The first scheme is the Nosé-Hoover (NH) method first proposed by Hoover [16]. Hamilton’s equations of motion are extended by the introduction of a thermostat variable \(\zeta\):

\[
\dot{r}_i = \frac{p_i(t)}{m_i},
\]

\[
\dot{p}_i = F_i - \zeta p_i,
\]

\[
\dot{\zeta} = \frac{1}{M_{\text{NH}}} \left( \sum_{i=1}^{N} \frac{p_i^2}{2m_i} - 3(N-1)k_B T \right).
\]

(2.28)

(2.29)

(2.30)

The variable \(\zeta\) is as a ‘thermostat coordinate’ that controls the transfer of heat energy between a heat bath and the system. If its value is zero then no heat is transferred. The rate of change of heat transfer is given by the time differential of \(\zeta\), i.e. \(\dot{\zeta} = \frac{d\zeta}{dt}\).

The parameter \(M_{\text{NH}}\) is the effective mass or inertia of the thermostat. It controls the rate of heat transfer between the heat bath and the particles. For a given temperature difference between the heat bath and the system, large \(M_{\text{NH}}\) results in a slow rate transfer of heat between the bath and the particle. Conversely, the rate of heat transfer is high when small \(M_{\text{NH}}\) is small.

The thermostat mass is related to a timescale \(\tau_{\text{NH}}\) for the relaxation of the thermostat:

\[
M_{\text{NH}} = 3(N-1)k_B T \tau_{\text{NH}}^2.
\]

(2.31)

The timescale \(\tau_{\text{NH}}\) corresponds to the time over which any instantaneous temperature fluctuations equilibrate when the system responds to change in temperature imposed by the heat bath. The value of \(\tau_{\text{NH}}\) is chosen such that the distribution of momenta is approximately the Maxwell-Boltzmann distribution (see section 2.6.5).

For the NH method the following quantity is approximately conserved during the MD simulation:

\[
\mathcal{H}_{\text{NH}} = K_N(p^N) + V_N(r^N) + \frac{M_{\text{NH}}\zeta^2}{2} + 3(N-1)k_B T \eta,
\]

(2.32)

where \(\eta = \zeta\). The energy \(\mathcal{H}_{\text{NH}}\) is not a true Hamiltonian as the NH equations of motion (equations 2.30) cannot be derived from it. It is sometimes called the extended energy of the system and its conservation is checked to ensure the simulations are numerically stable [17]. As NH equations are non-Hamiltonian, there are no true symplectic integrators to solve them.

The numerical integration scheme used for the NH equations is the explicit method proposed by Toxværd [18]. Starting from a configuration \(r^N(t), p^N(t)\) and \(\zeta(t)\), the mi-
crososcopic values at the next timestep are obtained as

\[ p_i(t + \frac{1}{2} \Delta t) = p_i(t) + \frac{1}{2} \Delta t (F_i(t) - \zeta(t)) , \]  
\[ r_i(t + \Delta t) = r_i(t) + \Delta t \frac{p_i(t + \frac{1}{2} \Delta t)}{m_i} , \]  
\[ \zeta(t + \Delta t) = \zeta(t) + \frac{\Delta t}{M_{NH}} \left( \sum_{i=1}^{N} \frac{p_i^2(t + \frac{1}{2} \Delta t)}{2m_i} - 3(N-1)k_B T \right) , \]  
\[ p_i(t + \Delta t) = \frac{p_i(t + \frac{1}{2} \Delta t) + \frac{1}{2} \Delta t F_i(t + \Delta t)}{1 + \frac{1}{2} \Delta t \zeta(t + \Delta t)} . \]  

Time reversibility is broken in this integration scheme in equation 2.36.

The Nosé-Poincaré (NP) thermostat was proposed as an extended phase space method for constant temperature molecular dynamics, where the equations of motion are derived from a Hamiltonian [17]. This method allows the use of numerical integration schemes that are both symplectic and time reversible to solve the equations, with the benefit of improved numerical stability when large fluctuations in the instantaneous temperature occur.

The Hamiltonian is

\[ H_{NP} = s \left[ K_N(p^N) + V_N(r^N) + \frac{\pi_s^2}{2M_{NP}} + 3(N-1)k_B T \ln s - H_0 \right] , \]  
where \( s \) and \( \pi_s \) are conjugate coordinates describing the state of the thermostat, \( M_{NP} \) is the artificial thermostat ‘mass’ akin to \( M_{NH} \), and \( H_0 \) is a constant chosen to ensure that \( H_{NP}(t=0) = 0 \).

The NP equations of motion cast in terms of the real momenta are

\[ \dot{r}_i = \frac{p_i(t)}{m_i} , \]  
\[ \dot{p}_i = F_i - \frac{\pi_s}{M_{NP}} p_i , \]  
\[ \dot{s} = s \frac{\pi_s}{M_{NP}} , \]  
\[ \dot{\pi}_s = H_0 - V_N(r^N) - \frac{\pi_s}{2M_{NP}} - 3(N-1)(1 + \ln s) . \]

These equations are numerically integrated with the symplectic scheme of Nosé [19]. In
terms of the real momenta the integrator is written as follows [20]:

\[
s(t + \frac{1}{2} \Delta t) = s(t) \left(1 + \frac{1}{2} \Delta t \frac{\pi_s(t)}{2M_{NP}} \right)^2,
\]

(2.42)

\[
\pi_s^* = \pi_s(t)/\left(1 + \frac{1}{2} \Delta t \frac{\pi_s(t)}{2M_{NP}} \right),
\]

(2.43)

\[
p_i(t + \frac{1}{2} \Delta t) = \frac{s(t)}{s(t + \frac{1}{2} \Delta t)} p_i(t) + \frac{1}{2} \Delta t F_i(t),
\]

(2.44)

\[
r_i(t + \Delta t) = r_i(t) + \Delta t \frac{p_i(t + \frac{1}{2} \Delta t)}{m_i},
\]

(2.45)

\[
\pi_s^* = \pi_s^* + \Delta t \left[K_N(p_i(t + \frac{1}{2} \Delta t)) - \frac{1}{2} (V_N(r^N(t)) + V_N(r^N(t + \Delta t))
\right.
\]

\[
- 3(N - 1) k_B T (1 + \ln s(t + \frac{1}{2} \Delta t)) + \mathcal{H}_0],
\]

(2.46)

\[
s(t + \Delta t) = s(t + \frac{1}{2} \Delta t) \left(1 + \frac{1}{2} \Delta t \frac{\pi_s^*}{2M_{NP}} \right)^2,
\]

(2.47)

\[
\pi_s(t + \Delta t) = \pi_s^* / \left(1 + \frac{1}{2} \Delta t \frac{\pi_s^*}{2M_{NP}} \right),
\]

(2.48)

\[
p_i(t + \Delta t) = \frac{s(t + \frac{1}{2} \Delta t)}{s(t + \Delta t)} \left(p_i(t) + \frac{1}{2} \Delta t F_i(t) \right).
\]

(2.49)

This integration scheme is both symplectic and time reversible.

### 2.4.2. Monte Carlo

Monte Carlo (MC) algorithms solve mathematical problems using random numbers to yield a stochastic solution. The MC was developed to simulate systems in statistical physics by Neumann, Ulam and Metropolis [21], whose work in the 1940s at Los Alamos National Laboratory concerned the diffusion of neutrons through materials.

The MC method works by generating large numbers of representative configurations from a statistical ensemble. Macroscopic thermodynamic quantities are then calculated as ensemble averages over these configurations.

MC simulations only generate configurational data, i.e. \( r^N \), for the state of the system. Although dynamical MC algorithms exist [22], they are not employed in this thesis. The MC simulation method is preferred over the MD method for the study of systems at thermodynamic equilibrium when only static configurational data are of interest.

We consider MC algorithms for simulating in two ensembles, namely the canonical and isobaric-isothermal ensembles.

**Canonical ensemble Monte Carlo**

Configurations from the canonical ensemble are sampled using the Metropolis-Hastings MC algorithm [23, 24]. This produces statistically representative configurations from the
NVT-ensemble.

A configuration with energy $E_{\text{init}}$ is updated via a random displacement to a particle’s position, known as a trial move. In the absence of external fields, the energy of a configuration is the total interaction energy $V_N(r^N)$. The particle is moved to a new position randomly chosen within a cube of sides $l$ centred on its original position. This yields a new configuration with energy $E_{\text{trial}}$.

The trial move is accepted or rejected, i.e. the initial configuration is restored, depending on the energy difference between the configurations. If $E_{\text{init}} - E_{\text{trial}} \geq 0$ the move is always accepted and the trial configuration becomes the new configuration for the system. If $E_{\text{init}} - E_{\text{trial}} < 0$ then the move is accepted with probability:

$$\exp\left[\beta(E_{\text{init}} - E_{\text{trial}})\right]. \quad (2.50)$$

In practice this is achieved by comparing equation 2.50 to a uniform random deviate in $[0,1]$ (see section 2.6.4 on random numbers).

A set of $N$ trial moves is known as an MC sweep. The percentage of accepted moves is tuned to be 50% by adjusting the MC step size $l$ after every sweep during the equilibration phase.

**Isobaric-isothermal ensemble Monte Carlo**

The isobaric-isothermal MC algorithm is that of McDonald [25]. Each MC sweep consists of on average $N - 1$ trial particle moves and a single volume change. The trial volume change for a configuration consists of a random walk in ln $V$. If the initial volume is $V_{\text{init}}$, the new volume $V_{\text{trial}}$ is randomly generated from a region of ln $V$ centred on ln $V_{\text{init}}$ and of size $\Delta \ln V$. The trial configuration is generated by scaling the simulation box sides and each component of the particle positions by $(V_{\text{trial}}/V_{\text{init}})^{1/3}$.

A trial volume change is accepted with probability:

$$\min\left\{1, \exp\left[-\beta(E_{\text{trial}} - E_{\text{init}} + P(V_{\text{trial}} - V_{\text{init}}) + (N + 1)\ln\left(\frac{V_{\text{trial}}}{V_{\text{init}}}\right)\right]\right\}. \quad (2.51)$$

The particle move step size $l$ and the volume change size $\ln V$ are adjusted so the acceptance ratios are respectively 25% and 50% for each move. This algorithm generates configurations from the NPT-ensemble with the correct statistical weights.

**2.4.3. Brownian dynamics**

Brownian dynamics (BD) simulation techniques are appropriate for systems where there is a large separation between timescales of different motions in the system. A good example for this is the motions of colloid and solvent particles in a colloidal dispersion.
The solvent particles move on atomistic timescales, whereas the motion of the colloids
is on the timescale of seconds. A MD simulation with explicit modelling of both the
solvent and colloidal particles would require a timestep smaller than the shortest vibra-
tional timescale of the solvent motions, and very long simulation length to capture the
dynamics of the colloids. Usually it is just the motions of the colloids that are of inter-
est, therefore it is both onerous and computationally difficult to deal with the solvent
molecules in this manner.

The solution offered by the BD technique is to omit the particles with fast motions
from the simulation, and to treat their effect on the other particles separately with ran-
dom forces and frictional damping. The simplest example of a BD simulation is the
method of Ermak and Yeh [26, 27]. Particle positions are updated via

\[
\mathbf{r}_i(t + \Delta t) = \mathbf{r}_i(t) + \frac{D}{k_B T} \mathbf{F}_i(t) \Delta t + \delta \mathbf{r}^G_i ,
\]

(2.52)

where \( \mathbf{r}_i \) are the positions of the particles with slow modes of motion, and \( D \) is their
diffusion coefficient through the fast particles. The \( \delta \mathbf{r}^G_i \) term represents random dis-
placements of the particles due to collisions with the solvent particles during the time
\( \Delta t \). These displacements are drawn from a Gaussian distribution with zero mean and
variance \( 6D \Delta t \), in order to obey the fluctuation-dissipation theorem [28].

2.5. Pair-potentials and models

In the simulations particles interact via spherically symmetric pairwise potentials. The
potentials define the interaction between two particles as a function of their separation
distance \( r \). The pair potentials are all written as combinations of inverse power law,
exponential and Gaussian functions of \( r \).

For particles interacting with the pair-potentials, the total interaction energy is given
by the sum of all the pair interactions \( u(r) \) between the particles:

\[
V_N(\mathbf{r}^N) = \sum_{i=1}^{N} \sum_{j \geq i}^{N} u(r_{ij}) ,
\]

(2.53)

where \( r_{ij} \) is the distance between the centres of particles \( i \) and \( j \). The potentials \( u(r) \) are
characterised by an energy scale for the strength of the interaction \( \epsilon \), and a lengthscale
parameter \( \sigma \).
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Figure 2.1: The pairwise potentials. (a) IPL, (b) LJ, (c) Morse, (d) Yukawa, (e) AO, (f) CRVT, (g) Wahnström binary LJ and (h) KA binary LJ. Lengths and energies are normalised by $\sigma$ and $\epsilon$ respectively, which are the natural length and energy scales of the potentials.
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2.5.1. Inverse power law potentials

Inverse power law (IPL) potentials are written as

\[ u_{\text{IPL}}(r) = A\varepsilon \left( \frac{\sigma}{r} \right)^n, \quad (2.54) \]

where \( n \) is a positive number [29]. If the energy scale \( \varepsilon \) is positive, the potential is purely repulsive. A singularity occurs at \( r = 0 \), and the potential monotonically decreases as \( r \) increases. If \( \varepsilon \) is negative the potential is attractive. The exponent \( n \) sets the range and strength of the interaction. An example IPL potential is shown in figure 2.1(a).

2.5.2. The Lennard-Jones potential

The Lennard-Jones (LJ) potential was introduced by Lennard-Jones in 1924 to describe the interaction between argon atoms in a gas [30]. It consists of an attractive IPL potential to describe the London dispersion interactions, and a repulsive IPL potential to model the Pauli repulsions at short ranges. In its usual 12-6 form, it is written as

\[ u_{\text{LJ}}(r) = 4\varepsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right]. \quad (2.55) \]

The potential is shown in figure 2.1(b). The LJ potential is extensively used in computer simulations to model the interactions in a variety of systems, including simple liquids, colloids, and glass-formers. Example LJ parameters for liquid argon are \( \sigma = 0.3345 \text{nm} \) and \( \varepsilon/\kappa_B = 125.7 \text{K} \) [31].

2.5.3. The Morse potential

The Morse potential was introduced to describe the interactions between two nuclei in a diatomic molecule [32]. It consists of two exponentials describing short-range repulsive and long-range attractive forces:

\[ u_{\text{M}}(r) = \varepsilon_{\text{M}} \exp[\rho_0 \sigma(1 - r/\sigma)] \exp[\rho_0 \sigma(1 - r/\sigma)] - 2. \quad (2.56) \]

The parameter \( \sigma \) sets the separation of two particles at mechanical equilibrium, and \( \rho_0 \) determines the range of the interaction. The parameter \( \varepsilon_{\text{M}} \) is the strength or well-depth of the interaction at \( r = \sigma \).

The Morse potential is commonly used to simulate large ensembles of atomic and molecular particles, where \textit{ab initio} and density functional theory quantum methods are computationally expensive. Example values of the range for physical systems are \( \rho_0 \sigma = 3.15 \) for sodium, \( \rho_0 \sigma = 3.17 \) for potassium, and \( \rho_0 \sigma = 13.62 \) for \( \text{C}_{60} \) molecules [33, 34]. The attractive well of the Morse potential has similar curvature to the LJ potential for...
\( \rho_0 \sigma = 6 \) \cite{35}. The Morse potential is used in this thesis to model colloidal interactions (chapter 4).

### 2.5.4. The Yukawa potential

The Yukawa potential was first introduced to describe the interaction between fermions \cite{36}. It takes the form of an exponentially screened Coulomb potential between two charged particles:

\[
\mathcal{U}_Y(r) = \varepsilon_Y \exp\left[\frac{-\kappa \sigma (r/\sigma - 1)}{r/\sigma}\right],
\]

(2.57)

where \( \kappa \) is the inverse Debye-Hückel screening length and \( \varepsilon_Y \) is the potential when \( r = \sigma \).

The Yukawa potential is frequently used to describe the electrostatic repulsion between charged colloids, where it is known as the Derjaguin-Landau-Verwey-Overbeek (DLVO) potential \cite{37, 38}. From the DLVO potential, the contact potential between two colloids with equal charge \( Z \) is

\[
\beta \varepsilon_Y = \frac{Z^2}{(1 + \kappa \sigma/2)^2} \frac{\lambda_B}{\sigma},
\]

(2.58)

where the colloid diameter is \( \sigma \) and \( \lambda_B \) is the Bjerrum length.

### 2.5.5. The Asakura-Oosawa potential

The Asakura-Oosawa (AO) potential was introduced to describe the effective pair potential that arises between two spheres immersed in a solution of smaller rigid bodies \cite{39}. The potential has a hard core ensuring the solute spheres do not overlap, and a short-range attraction over the lengthscale of the solvent particles.

The interaction is purely entropic in origin: states that minimise the ‘depletion volume’ of the solvent, or depletant, bodies\(^3\) are favoured as they are maximal in entropy. This is because the translational entropy of the depletant particles is maximised.

The form for the AO potential for colloidal dispersions with polymer depletants is \cite{40}

\[
\beta \mathcal{U}_{\text{AO}}(r) = \begin{cases} 
\infty & \text{for } r \leq \sigma, \\
-\phi_P \frac{(1+q)^3}{q} & \text{for } \sigma < r \leq \sigma + (2R_G), \\
\times \left[ 1 - \frac{3r}{2(1+q)\sigma} + \frac{r^3}{2(1+q)^3\sigma^3} \right] & \text{for } \sigma < r \leq \sigma + (2R_G), \\
0 & \text{for } r > \sigma + (2R_G),
\end{cases}
\]

(2.59)

where \( \phi_P \) is the reservoir volume fraction of the depletant polymers and \( R_G \) is the radius of gyration of the polymers. The number \( q = 2R_G/\sigma \) is the polymer-colloid size ratio.

\(^3\)The depletion volume is the volume that the depletant bodies cannot access when the two solute spheres encroach by distances smaller than the typical solvent particle size.
where \( \sigma \) is the diameter of the colloids.

### 2.5.6. The CRVT potential

The Chacón-Reinaldo-Falagán-Velasco-Tarazona (CRVT) potential was introduced as a simple pair potential for sodium \([41, 42]\). The model is parameterised as to match face-centred cubic (FCC) and body-centred cubic (BCC) crystal energies derived from local density approximation density functional theory \([43]\). The potential consists of an exponential repulsive and a Gaussian attractive term:

\[
    u_{\text{CRVT}}(r) = A_0 \exp[-ar] - A_1 \exp[-b(r - R_1)^2].
\]  

(2.60)

The values of the constants are \( A_0/k_B = 5.0823 \times 10^6 \text{ K}, \ a = 22.322 \text{ nm}^{-1}, \ A_1/k_B = 2133.1 \text{ K}, \ b = 21.4 \text{ nm}^{-2}, \) and \( R_1 = 0.35344 \text{ nm}. \)

### 2.5.7. Wahnström and Kob-Andersen binary Lennard-Jones mixtures

Finally we consider two models for binary metallic glasses based on LJ potentials, namely the Wahnström and Kob-Andersen (KA) models \([44, 45]\). Two species of particles, \( A \) and \( B \), interact with pairwise LJ potentials of the form

\[
    u_{\alpha\beta}(r) = 4\varepsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right],
\]  

(2.61)

where \( \alpha, \beta \in \{A, B\} \).

The values of the parameters are \( \sigma_{AB} = 11/12\sigma_{AA}, \ \sigma_{BB} = 5/6\sigma_{AA}, \) and \( \varepsilon_{AA} = \varepsilon_{AB} = \varepsilon_{BB} \) for the Wahnström mixture. These parameters obey the Lorentz-Berthelot mixing rules \([46, 47]\), i.e. \( \sigma_{AB} = \frac{1}{2}(\sigma_{AA} + \sigma_{BB}) \) and \( \varepsilon_{AB} = \sqrt{\varepsilon_{AA}\varepsilon_{BB}} \).

The parameters for the KA mixture are \( \sigma_{AB} = 0.8\sigma_{AA}, \ \sigma_{BB} = 0.88\sigma_{AA}, \) and \( \varepsilon_{AB} = 1.5\varepsilon_{AA}, \ \varepsilon_{BB} = 0.5\varepsilon_{AA} \). No physical manifestation for the Wahnström mixture was proposed \([44]\), however the KA mixture was suggested as a model for amorphous Ni\(_{80}\)P\(_{20}\) alloy \([45, 48]\).

These two-component LJ mixtures are chosen as crystallisation is rare in the supercooled phase. The mixtures can be stabilised for extended periods in MD simulations, however crystallisation can occur at long times \([49–51]\).
Chapter 2. Methodology and Simulation Details

2.6. General simulation properties

2.6.1. Geometry and periodic boundary conditions

Simulations are performed in three dimensions in cuboid boxes of sides $L_x$, $L_y$ and $L_z$. Orthogonal unit vectors $\hat{x}$, $\hat{y}$ and $\hat{z}$ point in directions along the edges of the simulation box. In order to minimise surface effects periodic boundary conditions (PBCs) are employed. The cuboid box is replicated throughout space on an infinite lattice. The motion of a particle in the origin cuboid is replicated within all of the periodic images of the cuboid across the lattice. As one particle leaves the origin cuboid, it is replaced by one of its periodic images entering from other side of the origin cuboid. A particle interacts with the closest periodic images of the $N-1$ other particles, known as the minimum image convention [5]. PBCs are illustrated for a two-dimensional system in figure 2.2.

The use of cuboid simulation boxes with periodic boundary conditions imposes a limit on the maximum lengthscale for any phenomena studied. If $L$ is the smallest of the cuboid sides, the maximum wavelength of any collective fluctuation of the particles is $L$. This limit must be considered when studying phenomena that occur over large length scales, such as critical fluctuations near the liquid-gas critical point, capillary waves along interfaces, or dynamical heterogeneities in supercooled liquids.

2.6.2. Truncated potentials

In order to speed up the calculation of potential energies and forces between particles it is common to only evaluate the interactions for particles separated by distances up to a maximum cut off distance $r_{tr}$. This is known as truncating the potential and it reduces the total number of pair interactions that need to be calculated. Employing a truncated
potential with cell and Verlet lists (described in the next section) in a simulation code yields a significant real-time speed up to perform the calculation.

The philosophy for truncating a potential is that the long-range contribution of a pair-potential to the total energy of the system is small, and therefore only has a small effect on the properties of the system. This is the case for the potentials described in section 2.5 and employed in this thesis, which all quickly decay to zero at long ranges \(^4\). Exceptions not considered here are Coulombic, gravitational and hydrodynamic interactions that decay as \(r^{-1}\). The long-range contributions of these interactions to the potential are significant and need to be calculated with Ewald-type summations if using PBCs [5, 54–56].

Three methods are used to truncate a potentials in the simulations, namely the simple truncation, truncation and shift, and Stoddard-Ford methods.

**Simple truncation**

For the simple truncation method all interactions beyond a cut off distance \(r_{tr}\) are ignored. The potential becomes

\[
 u^T(r) = \begin{cases} 
 u(r) & \text{for } r \leq r_{tr}, \\
 0 & \text{for } r > r_{tr}.
\end{cases}
\]  

(2.62)

**Truncation and shift**

Truncated potentials \(u^T(r)\) are discontinuous at \(r_{tr}\). The discontinuity is problematic in MD simulations as energy is not conserved when two particles cross the separation boundary defined by \(r_{tr}\). The discontinuity in energy can be avoided by shifting the potential at short ranges by the value of the potential at the discontinuity \(u(r_{tr})\). This yields a truncated and shifted potential with the form

\[
 u^{TS}(r) = \begin{cases} 
 u(r) - u(r_{tr}) & \text{for } r \leq r_{tr}, \\
 0 & \text{for } r > r_{tr}.
\end{cases}
\]  

(2.63)

The truncated and shifted potential is continuous for \(r > 0\).

\(^4\)An Ewald summation has been proposed for the Yukawa potential due to its slowly decaying tail [52, 53]. However a short-screening length is considered for systems in this thesis, and the Yukawa potential is truncated in the simulations at a range where its value is small.
The Stoddard-Ford method

If using the truncation and shift method, there is no guarantee that the resultant force will be continuous at \( r_{tr} \). A discontinuous force can also cause instabilities long-time MD simulations. This is because two particles feel an instantaneous impulse when their separations cross the interaction range boundary \( r_{tr} \).

Stoddard and Ford introduced a method to truncate, smooth and shift the LJ potential to ensure continuity of both the potential and the force across \( r = r_{tr} \). The method works by adding a quadratic term in \( r \) and a constant to the potential.

Here we present the Stoddard-Ford method in a generalised form. The pairwise force is

\[
F_{SF}(r) = -\frac{\partial u_{SF}}{\partial r}(r) = \begin{cases} 
-\frac{\partial u}{\partial r}(r) + \frac{r}{r_{tr}} \frac{\partial u}{\partial r}(r_{tr}) & \text{for } r \leq r_{tr} , \\
0 & \text{for } r > r_{tr} .
\end{cases}
\]

A linear term has been added for \( r \leq r_{tr} \) to ensure continuity at \( r = r_{tr} \). Integrating and setting the potential equal to zero at \( r_{tr} \) yields:

\[
u_{SF}(r) = \begin{cases} 
u(r) + \frac{r^2}{2r_{tr}} \frac{\partial u}{\partial r}(r_{tr}) - u(r_{tr}) - \frac{r_{tr}}{2} \frac{\partial u}{\partial r}(r_{tr}) & \text{for } r \leq r_{tr} , \\
0 & \text{for } r > r_{tr} . \end{cases}
\]

The potential and force are continuous for \( r > 0 \).

2.6.3. Neighbour lists

Truncated potentials are zero beyond the truncation distance so only the interactions between particles separated by less than \( r_{tr} \) need to be calculated. The simplest algorithm to calculate the pair interactions first calculates the separations between all pairs of particles. This scales as \( O(N^2) \) limiting both the size and speed of the computer simulation - all before the interaction is even calculated! Therefore it is desirable to limit the number of pairs for which the separation has to be calculated in order to check the condition \( r_{ij} < r_{tr} \).

Two methods are considered to reduce the number of calculations for pair separations. Both methods work by maintaining lists of particles that occupy a volume in space, either relative to the coordinate system or to a particle’s position. The use of each method depends on the type of simulation being conducted (MD, BD or MC). The methods described are covered in references [5, 6].
Chapter 2. Methodology and Simulation Details

(a) (b)

Figure 2.3: Neighbour lists for reducing the number of pair separation calculations. 2D figures can be considered as slices of 3D simulation. (a) Cell list: The simulation box is decomposed into cells with side lengths greater than the potential truncation length $r_{tr}$. At each potential or force calculation all the particles are sorted into the cells. Pair separations for a particle in cell $i$ are only calculated for particles within cell $i$ and within the neighbouring (shaded) cells. (b) Verlet list: A list is maintained of all the particles within a sphere of radius $r_v$ around each particle. Pair separations are only calculated for the particles within the list, and henceforth interactions for particles with the sphere of radius $r_{tr}$. Figures adapted from [6].

Cell lists

A cell list divides the simulation cuboid into cells of equal volume. The minimum length of any cell side is $r_{tr}$. Particles are first sorted into cells and subsequently pair separations are only calculated for particles within the same or the immediately neighbouring cells. The interactions are then calculated for those pairs where $r_{ij} < r_{tr}$.

The cell list needs to be updated each time a particle crosses a cell boundary, which is a frequent occurrence for liquid and disordered systems. The computational overhead of employing a cell list scales as $O(N)$ in the system size. The cell list offers improvements in speeds for MD, BD and MC simulations, as well as for calculations of neighbour networks as described in chapter 3.

Verlet lists

A Verlet list maintains a record of all the particles within a sphere of radius $r_v$ around a particle. The radius $r_v$ is greater than the truncation distance $r_{tr}$. Filling the Verlet lists for all the particles is an order $O(N^2)$ operation in time, but the lists need only be updated when the sum of the two largest displacements of the particles since the previous update is greater than $r_v - r_{tr}$.

5A truncated and shifted LJ potential with $r_{tr} = 2.5\sigma$ has a discontinuous force at $r = r_{tr}$, for instance, but the Weeks-Chandler-Andersen (WCA) form of the LJ potential does not [57].
In practice a cell list outperforms a Verlet list for large systems, as the $O(N^2)$ creation of the Verlet lists dominates the calculation. However, it is possible to fill Verlet lists using the particles in a cell list \(^6\), yielding a combined algorithm with overhead $O(N)$. This algorithm is preferred for MD and BD simulations as the volume over which pair separations must be calculated is smaller than when using only a cell list.

For MC simulations of liquids, $r_v$ needs to be larger than the particle moves in order that the Verlet list does not need to be updated at every move. This can increase the volume of the Verlet spheres beyond that of the volume $27r_v^3$, i.e. the volume for which a list needs to be maintained if using just a cell list. Therefore better performance is often obtained in MC simulations if only a cell list is maintained, rather than a combination of a cell and Verlet list \([6]\). For our MC simulations only a cell list is employed.

### 2.6.4. Random numbers

Random numbers are required for the stochastic components of the MC and BD simulation techniques, and are also required to generate an initial configuration for the system (see following section). Calculations on computers are in principle deterministic, at least to the precision of round-off errors, but computers can be programmed to generate sequences of pseudo-random numbers using random number generators. The method employed in this thesis is the L’Ecuyer with Bays-Durham shuffle algorithm presented in Numerical Recipes \([59, \text{p. 280}]\), known as ran2. This algorithm is hypothesised to pass all statistical tests for random numbers within the limits of floating-point precision \([59, \text{p. 281}]\).

### 2.6.5. Initial configuration

The initial configuration for a simulation is the set of positions $\mathbf{r}_0^N$ of all the particles. Initial momenta $\mathbf{p}_0^N$ are also required if performing MD simulations. These must be generated before a simulation can commence.

Depending on the system being studied, the initial configuration is generated in various ways. Particle positions are defined by either randomly inserting particles into the simulation box, or by initialising particles on the sites of a crystal lattice. Initial momenta are generated by drawing velocities randomly from a Maxwell-Boltzmann distribution of a set temperature.

**Positions by random insertion**

Particles are inserted sequentially into a simulation box in random positions yielding a configuration with density $\rho$. To ensure numerical stability on commencing the sim-

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\(^6\)The cell side lengths must now be greater than $r_v$. 
Chapter 2. Methodology and Simulation Details

Figure 2.4: Initialising particle positions on crystal lattices. (a) SC crystal with 8 particles. (b) BCC crystal with 16 particles. (c) FCC crystal with 32 particles. (d) HCP crystal with 8 particles in a cuboid simulation box.

ulation, it is ensured that no two particles are separated by a distance shorter than a maximum distance of approach \( r_{\text{ol}} \). If a randomly generated trial position for the insertion of a new particle results in a separation with an existing particle of \( r < r_{\text{ol}} \), the trial position is rejected and a new one is generated.

This algorithm becomes unfeasible when \( r_{\text{ol}} \) is large or if the density is high, as particle insertions are rejected with high probability.

Positions on crystal lattices

For high density systems the initial positions \( \mathbf{r}_0^N \) of the particles are defined by the lattice sites of simple cubic (SC), body-centred cubic (BCC), face-centred cubic (FCC) and hexagonal close packed (HCP) crystals. The SC, BCC and FCC crystal lattices fit into cubic simulation boxes and contain \( n_{\text{xtal}}^3 \), \( 2n_{\text{xtal}}^3 \) and \( 4n_{\text{xtal}}^3 \) lattice sites respectively, where \( n_{\text{xtal}} \) is a positive integer.

HCP crystals have non-cubic unit cells that cannot pack into a cubic simulation box without leaving voids. HCP crystals are initialised in cuboid simulation boxes with side lengths \( L_x, L_y = \sqrt{3} L_x \) and \( L_z = \sqrt{6} L_x \). The total number of lattice sites is \( n_{\text{xtal}}^3 \).

Velocities drawn from the Maxwell-Boltzmann distribution

Initial momenta for MD simulations are drawn from the Maxwell-Boltzmann distribution for the momentum vectors of ideal gas particles. Each component of the momentum is a normal distribution with zero mean and variance \( mk_B T \), i.e.

\[
f(p_{\alpha,i}) = \frac{1}{\sqrt{2\pi m_i k_B T}} \exp \left[ -\frac{p_{\alpha,i}^2}{2m_i k_B T} \right],
\]

where \( p_{\alpha,i} \) is each component of the momenta for particle \( i \), and \( f(p_{\alpha,i}) \) is the probability density.
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The total linear momentum is set to zero, i.e. \( \mathbf{P} = 0 \), by removing the drift of the centre of mass.

**Initialisation of molecular dynamics thermostats**

The initial states of the thermostats in \( NVT - MD \) simulations are \( \zeta = \dot{\zeta} = 0 \) when using the \( NH \) thermostat, and \( s = 1, \pi_s = 0 \) when employing the \( NP \) thermostat.

2.6.6. Equilibration

On commencing a simulation it is necessary to ensure that the system equilibrates before sampling time and ensemble averages. If equilibration is not achieved, the averages will drift during the simulation run and the system is said to age. Details of the equilibration processes are highlighted in the ‘simulation details’ sections of later chapters, but the basic premise is to run the simulation for a number of multiples of longest relaxation time of the system before beginning to sample averages. It is also checked that there is no drift in the thermodynamic properties, correlation functions and cluster distributions across the sampled configurations and trajectories.

2.6.7. Parallelisation of simulations

The \( MD \) simulations are parallelised in order to reduce the physical time taken for the computation. This is achieved by spreading the \( MD \) force calculations across many CPU processing units in a multi-core computing architecture. The method used is the \( A2 \) atomic-decomposition algorithm described in reference [60].

For a simulation utilising \( n_p \) CPU cores, each core is assigned a subset \( N/n_p \) particles. Each core calculates the forces between its \( N/n_p \) particles and approximately half of the particles within its own particles’ interaction ranges. The remaining forces are calculated by other the cores and are received as communications from them. Likewise, the forces acting on particles not contained within core’s set of \( N/n_p \) are propagated out to the other cores in the system as required.

The \( MPICH \) library for the message parsing interface (\( MPI \)) standard is used for communication between CPU cores [61].

2.7. Reduced units

It is common to present simulation-derived quantities in terms of some fundamental units for the system under consideration. This means that the data presented are usually within a few orders of magnitude of unity. There are also technical advantages to be gained by calculating in reduced units within the simulation code. The advantages include faster calculations, better numerical stability and easier detection of errors.
Throughout this thesis all quantities that are quoted without an International System of Units (SI) unit are reduced by the natural mass $m$, length $\sigma$ and energy $\varepsilon$ scale for the system under consideration. The following reduced static and dynamic quantities are derived from their real values with respect to these parameters,

- **mass** $m^* = m' / m$
- **length** $r^* = r / \sigma$
- **density** $\rho^* = \rho \sigma^3$
- **energy** $E^* = E / \varepsilon$
- **temperature** $T^* = k_B T / \varepsilon$
- **pressure** $P^* = P \sigma^3 / \varepsilon$
- **time** $t^* = (\varepsilon / m \sigma^2)^{1/2} t$

Here the superscript asterisk is used to denote a reduced unit. For brevity we choose to omit the asterisk from reduced quantities from here onwards. The reader should always bear in mind that the values need not correspond directly to any real values observed in experiments. Real variables are highlighted by the inclusion of an appropriate SI or real unit.

An expanded discussion on the benefits of reduced units can be found in the appendix of reference [5].

### 2.8. Summary

In this chapter the theoretical formalism for the systems that are studied in this thesis was summarised. The concepts introduced will be repeatedly revisited when discussing structural and dynamical correlations in chapter 3, the behaviour of colloidal clusters in chapter 4, liquid-gas interfaces in chapter 5, and supercooled liquids in the latter chapters of this thesis.

The technical details of the computer simulations used to generate data to study these systems was also covered. In the following chapter structural and dynamical correlation functions are reviewed, before introducing and testing the topological cluster classification (TCC) algorithm, which forms the basis for structural and dynamical investigations in future chapters.
2.9. Bibliography


[61] MPICH - A Portable Implementation of MPI.
CHAPTER 3

Identification of Structure in Condensed Matter

3.1. Introduction

Research into the structure of disordered systems, such as liquids, interfaces and cluster fluids, has a rich history. Early studies focused on pair distribution functions as these were readily accessible from experiments using scattering techniques. The experimental results inspired the development of theories with the capability to predict the radial distribution functions for disordered states. The most famous example of such a theory is perhaps the Percus-Yevick closure of the Ornstein-Zernike relation, from which the radial distribution function for the hard sphere fluid can be calculated [1].

Efforts to understand the structure of liquids in finer detail than the pair correlations of the particle density were pioneered by Bernal, Rahman and Finney [2–4]. These authors studied the properties of the Voronoi cells in liquids, which are convex polyhedra that contain all points in space closer to one particle than any other. The geometrical characteristics of each polyhedron depends on the position of the particle and its immediate neighbours. As such Voronoi cells provide information on higher-degree correlations of the particle density than two-body distribution functions.

The studies into Voronoi polyhedra were among some of the earliest research that characterised the structure of disordered systems in terms of the shapes formed by small clusters of particles. Many subsequent efforts have been made in this direction. and there are now several methods for quantifying structural correlations in disordered systems with clusters. We refer to a subset of these methods as topological methods if they identify clusters from topological features of the bond network formed by the particle locations and the connections between neighbouring particles.

Two topological methods that see frequent use today are the common neighbour analysis (CNA) introduced by Honeycutt and Andersen [5] and the Voronoi face analysis (VFA) from Tanemura et al. [6]. The CNA identifies the structural ordering around pairs
of particles in terms of shared (common) neighbour particles. The VFA technique is a generalisation of the early Voronoi cell studies. The structure around a single particle is characterised by the arrangement of its nearest neighbours and the bonds between them. This information is encoded by the shapes of the faces of the particle’s Voronoi cell. Both the CNA and VFA methods have been used to study phenomena including the melting and freezing of clusters [5], structural developments in supercooled liquids on cooling towards the glass transition [7–12], and crystallisation [6, 13, 14].

Complementary to the topological methods for identifying clusters, higher-order geometrical measures have also been developed to characterise the structure in disordered systems. We designate methods as geometrical if the structural order parameters are written as explicit functions of the particle positions. At the two-body level, the radial distribution function and structure factor would therefore be classed as geometrical methods, by this definition. The simplest example of a geometrical method that employs three-body information to characterise structure is perhaps the study of bond angle distributions [15, 16].

A powerful geometrical method was introduced by Steinhardt, Nelson and Ronchetti to characterise the arrangement of neighbouring particles around a central particle [17, 18]. A number of bond orientational order (BOO) parameters are defined that quantify the similarity between the directions from a particle to its neighbours and the spherical harmonic solutions to the Laplace equation. This method has been described as a kind of shape spectroscopy [18, 19].

BOO parameters have been applied for the study a variety of phenomena. Their original application was in a study on structural ordering in supercooled liquids [17, 18]. Depending upon the system under consideration, both icosahedral [20] and crystalline ordering [21] has been found by examining BOO parameters to develop on cooling towards the glass transition. Other researchers have employed BOO parameters to study structure at interfaces [22, 23] and in large clusters [24]. Arguably the most successful applications of BOO parameters however is as order parameters for crystallisation [25–29].

Many of the higher-order structural algorithms reviewed in this chapter have been employed for either experimental studies with granular materials, or in simulation studies. This is because obtaining configurational data to use with many of the higher-order structural detection methods from experiments on atomic or molecular systems remains extremely challenging.

Recent advances in experimental techniques on colloidal dispersions have delivered methods that allow measurement of real space configurational data for colloids. In particular, particle tracking software allows colloid positions to be extracted from images taken with either confocal or light microscopy [30]. This development means that the structure of experimental systems that display Brownian motion can now be analysed
with higher-order structural detection algorithms, and studies have been published on structure in colloidal gels [31], glasses [32] and critical fluctuations [33].

The breakdown of this chapter is as follows: The first part contains a review of some commonly used and more recently published methods to characterise the structure in a system beyond the level of pair correlations. The purpose of the review to provide the context for the development of the structural method that we employ in this thesis - the topological cluster classification (TCC) algorithm. The review allows us to draw comparisons between the TCC algorithm and some of the more established techniques. The review begins with a discussion of two-body density correlation functions, the radial distribution function and the static structure factor, section 3.4.

One common feature of many of the higher-order structure detection routines reviewed is that they require definition of the neighbours for each particle as an input into the algorithm. Section 3.5 contains details of two commonly used methods to define the neighbours of each particle, namely using a cut-off length or a Voronoi construction. The characteristics of each of these methods are discussed, and the need for the modified Voronoi algorithm which was introduced with the TCC method is highlighted [34]. The modified Voronoi method determines the neighbours independently of any length scale parameter and avoids some of the problems associated with using the standard Voronoi method.

In section 3.6 a number of higher-order structure detection methods that are used in the literature algorithms are reviewed. This includes the established VFA, CNA and BOO methods, and a number of other structure detection routines.

The final part of the chapter contains the methodology of the TCC algorithm, section 3.7. Detection routines are listed for a number of structures that are the ground state clusters of various commonly studied pair potentials. The technique is demonstrated with a structural analysis of Lennard-Jones (LJ) liquids and crystals.

### 3.2. Aims for the TCC algorithm

The introduction described how research into crystallisation, disordered states, interfaces and clusters has seen the development of a number of higher-order methods to quantify the structural arrangement of particles in a system. These methods offer greater sensitivity to structural features of a system than the information provided by pair correlation functions. There are a number of questions that may be posed, however, about the mechanisms of the detection routines and how the results should be interpreted. Throughout this thesis we are concerned with the following questions:

1. Is it possible to establish relationships between the phase and state behaviour of a system and local structural ordering of the particles?
2. Can the structural ordering be predicted from the interactions between the component particles?

3. Many of the higher-order methods reviewed here have an analysis that is limited to structures of a certain size, for example at the levels of a particle and its neighbours, or the common neighbours around pairs of particles. Should structures of different sizes also be considered, and if so how?

4. Given that the structures only have a microscopic spatial extent, how does any local structure identified relate to the macroscopic behaviour of a system displayed on long lengthscales?

5. Are domains of the system characterised by a particular structure related to inhomogeneous and spatially localised phenomena, such as dynamical heterogeneity or interfacial layering?

6. When a structure detection algorithm identifies an ordering with an unknown symmetry\(^1\), what should the physical interpretation be for these structures?

The TCC algorithm introduced by Williams and Royall is a tool that we will employ, either in its original form or through various extensions, to tackle these questions [31, 34]. This chapter contains a detailed description of the TCC algorithm and a set of extensions to detect the ground state clusters for two binary LJ models. While we begin to address these questions in this chapter, it is in later chapters that feature the results of studies designed to probe these questions and where the majority of our conclusions will be drawn.

The philosophy of the TCC algorithm draws heavily upon an idea proposed by Sir Charles Frank in a seminal paper from 1952 [35]. Frank was discussing the ability to stabilise metallic liquids below the melting temperature and proposed that collections of particles may preferentially adopt certain energy-minimising structures on short lengthscales. If the symmetry of the structures formed is incommensurate with that of the bulk crystal symmetry, he argued that the structures would inhibit crystallisation and stabilise the undercooled melt. The basis for this was that there must be a substantial rearrangement of the structures for crystallisation to proceed, and this operation would carry an energetic cost.

To demonstrate his idea Frank cited the example of the ground state clusters formed by 13 LJ particles in isolation. Arranging the particles at the centre and the vertices of a regular icosahedron yields a cluster with 8.4% lower interaction energy than for compact face-centred cubic (FCC) or hexagonal close packed (HCP) crystal clusters of

\(^1\)To cite a concrete example of this, a number of locally preferred structures found to form on the supercooling of liquids have an unknown symmetry [16].
13 particles. Assuming that the energy of the icosahedral arrangement remains as the lowest of the three arrangements in the disordered liquid environment, Frank inferred that icosahedral formations of the particles would be more prevalent than FCC and HCP arrangements in the supercooled liquid.

While Frank considered ground state cluster of 13 LJ particles in his example, the TCC algorithm considers the ground state clusters of other numbers of particles as well. The algorithm also considers the ground state clusters of systems other than LJ.

The TCC algorithm works by searching a configuration for structures of particles where the arrangement is similar to that of the particles in the ground state clusters of the interaction potential. The method therefore provides a direct link between the interactions in the system under consideration and any structural ordering that may be found.

The philosophy for the TCC favours no specific ‘origin’ particles for the clusters. Here an origin particle could be a central particle in the cluster or a bonded pair. This means that routines can be devised to detect clusters with disparate shapes and sizes where there may be no natural origin particles to base the detection routine upon. This stance differentiates the TCC method from many of the other structure detection methods reviewed in this chapter. The TCC algorithm presented here includes detection routines for ground state clusters of up to 13 particles for the potentials that are considered. Inclusion of detection routines for larger ground state clusters is possible, although the detection routines will necessitate an increasing length of computer code.

A basic summary of how the TCC algorithm works is as follows:

1. The neighbours of each particle are identified.
2. The neighbour network is searched for shortest-path rings of 3, 4 and 5 particles.
3. From the rings a set of structures, known as the ‘basic clusters’, are identified. The basic clusters are defined by the number of additional particles that are common neighbours of all the particles in a shortest-path ring.
4. Larger clusters are then identified by combining basic clusters together, perhaps with the addition of one or two separately bonded particles, according to a set of predefined rules. The method yields structures with bond networks with similar topology to the bond networks of the ground-state clusters.

Throughout this chapter we endeavour to highlight the strengths and weaknesses of the TCC method. Although the focus of this thesis is on disordered systems, the performance of different structure detection algorithms for identifying crystalline order will provide a useful benchmark for comparing the different methods. These tests are use-
ful as the local ordering of particles in a crystal is known \textit{a priori}, whereas this is not necessarily the case for a disordered system.

3.3. Local and global structure

Before beginning our review of structure detection methods we pause to define two pieces of terminology for how a structural information for a system may be presented.

\textit{Global} structure measures are defined when the measure is the spatial averaged across the whole system. These measures convey no specific information about the structure in a defined volume, other than that of the average structure of the whole system. Radial distribution functions are normally presented in this way, as are certain measures derived from cluster analyses such as the average number or density of clusters, and the fraction of particles detected within each cluster type.

\textit{Local} measures of structure quantify the structure in some finite locality or volume of the space. Examples of local measures include an individual particle’s coordination number, i.e. its number of nearest neighbours, one of its bond-orientational order parameters, or data describing specific clusters that it participates in.

3.4. Two body correlation functions

3.4.1. The radial distribution function

The radial distribution function, or pair correlation function, quantifies the structure at a fixed distance from a particle in terms of its deviation from a completely random density distribution. It is defined using the equilibrium 2-particle density

\[ \rho^{(2)}_{N}(r, r') = \langle \sum_{i} \sum_{j 
eq i} \delta(r - r_i)\delta(r' - r_j) \rangle \]

in the case of a homogeneous\(^2\) and isotropic system\(^3\) as \([1]\)

\[ g(r) = \frac{1}{N\rho} \int \rho^{(2)}_{N}(r, r') \, dr'. \]  \hspace{1cm} (3.2)

The integral extends over the entire volume of the system. Equation 3.2 is often expressed in terms of \(\delta\)-distributions as

\[ g(r) = \frac{1}{N\rho} \langle \sum_{i} \sum_{j \neq i} \delta(r - r_i - r_j) \rangle, \]  \hspace{1cm} (3.3)

\(^2\)A system is said to homogeneous if its physical properties are uniform across its volume. This is not the case, for example, in the vicinity of interfaces.

\(^3\)For an isotropic system the pair density \(\rho^{(2)}_{N}(r_1, r_2)\) can be written as a function of the magnitude of the separation between particles \(\rho^{(2)}_{N}(r_{12}), \) where \(r_{12} = |r_{12}| = |r_1 - r_2|. \)
where $i$ and $j$ are indices for the particles.

Integrals over $g(r)$ can be used to calculate various properties of the system. The average number of particles in the infinitesimal volume between distances $r$ and $r + dr$ from any particle is $4\pi \rho r^2 g(r)dr$. The total number of particles $n$ in the region formed by the intersection of two spheres of radii $r_1$ and $r_2$ is therefore

$$n = 4\pi \rho \int_{r_1}^{r_2} r^2 g(r)dr.$$  \hfill (3.4)

For systems with pairwise interactions the excess internal energy \cite{1} is

$$U^{sx} = 2\pi \rho N \int_{0}^{\infty} r^2 u(r)g(r)dr,$$  \hfill (3.5)

and the virial equation for the pressure is

$$\frac{\beta P}{\rho} = 1 - \frac{2\pi \beta \rho}{3} \int_{0}^{\infty} r^3 u'(r)g(r)dr.$$  \hfill (3.6)

In order to calculate $g(r)$ from real-space data, obtained for example from simulations or confocal microscopy of colloidal dispersions, it is necessary to discretise space in order to numerically evaluate the integral in equation 3.2. A histogram is populated with the separations of pairs of particles lying in the range $[\Delta r m, \Delta r (m + 1))$, where $m$ is a non-negative integer and $\Delta r$ is the width of the bins. The radial distribution function is approximated in this range as

$$g(r) = \frac{3}{4\pi \Delta r^3 ((m + 1)^3 - m^3) \rho (N - 1)} \left( \sum_{i} \sum_{j \neq i} \delta(r - r_{ij}) \right).$$  \hfill (3.7)

The discrete $\delta$-function here is unity if the separation between particles indexed by $i$ and $j$, $r_{ij} = |r_i - r_j|$, falls within $[\Delta r m, \Delta r (m + 1))$, and zero otherwise. Simulations sizes are always in practice much smaller than the thermodynamic limit so the correction $N - 1$ in the denominator ensures $g(r) \to 1$ at large $r$.

Although the definition of $g(r)$ in statistical mechanics (equation 3.2) is restricted to homogeneous, isotropic and equilibrium systems, it is possible to calculate a radial distribution function using equation 3.7 when these conditions are not met.

The behaviour of the radial distribution function is shown in figures 3.1(a)-(c) for three phases of the LJ model: gas, liquid and crystal. For the gas (figure 3.1(a)) $g(r)$ indicates that there is little structure. Strong short-range repulsions inhibit two particles from closely approaching one another and cause $g(r)$ to vanish. The peak at $r \approx 1$ is created by the attractions between the gas particles. For separations much greater than the range of the inter-particle interactions $g(r)$ attains the ideal-gas limit of $(1 - 1/N) \approx 1$. 
Figure 3.1: The radial distribution function $g(r)$ for three phases of the LJ model at $T = 1.0$. (a) Gas at $\rho = 0.01$, (b) liquid at $\rho = 0.85$, and (c) FCC crystal at $\rho = 1.2$. Note the different scales on the vertical axis. The strength of the correlations between the positions of pairs of particles is given by the magnitude of $g(r)$. Simulation details: molecular dynamics in the $NVT$-ensemble (Nosé-Hoover thermostat), $N = 2048$, with timestep $\delta t = 0.001$ and truncated and shifted potential with $r_{tr} = 2.5$.

This indicates that the structure at long length scales is completely random.

For a liquid a series of peaks and troughs emerge in the radial distribution function (figure 3.1(b)). These correspond to layering in the liquid structure creating ‘shells’ of neighbours around each particle. The correlations decay exponentially with increasing $r$ indicating that there is no long range order in the liquid. The volume up the first minimum is known as the coordination shell and integrating equation 3.4 up to this distance gives the coordination number (see later section on the coordination number, section 3.6.2).

In figure 3.1(c) the radial distribution function is displayed for a crystal. The regular arrangement of the particles on the FCC lattice leads to large peaks in $g(r)$. The positions of the peaks correspond to the separations if a particle is translated between lattice sites. At zero temperature the peaks are $\delta$-functions and these are smeared out by thermal fluctuations at non-zero temperature.

The radial distribution functions presented in figure 3.1 are global measures as $g(r)$ is averaged over all the particles in the system. It is possible to define a radial distribution function for a single particle, $i$, by removing the first sum in equation 3.7.

### 3.4.2. The static structure factor

The static structure factor is a quantity accessible with experimental scattering techniques. It measures the density response of a system initially at equilibrium to a small excitation by an external wave. It provides a natural representation of any periodicity in the density.
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The static structure factor is defined as [1]

\[ S(k) = \langle \frac{1}{N} \rho_k \rho_{-k} \rangle. \]  
(3.8)

The quantity \( \rho_k \) is the Fourier transform of the microscopic density \( \rho(r) \):

\[ \rho_k = \int \rho(r) \exp(-i \mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r} = \sum_i \exp(-i \mathbf{k} \cdot \mathbf{r}_i). \]  
(3.9)

Note that \( i \) takes two definitions in this equation. In the sum \( i \) is used to index the particles and their corresponding positions \( \mathbf{r}_i \) and in exponential function it is the imaginary unit defined as \( i^2 = -1 \).

In the case of an equilibrium homogeneoues fluid the limit of \( S(k) \) for small \( k \), i.e. long wavelength excitations, is related to the isothermal compressibility of the system by

\[ \lim_{k \to 0^+} S(k) = \rho k_B T \kappa_T. \]  
(3.10)

In the isotropic and homogeneous case, the angularly averaged structure factor is related to the radial distribution function via its Fourier transformation [1]:

\[ S(k) = 1 + \rho \int g(|r|) \exp(-i \mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r}, \]  
(3.11)

where \( k = |\mathbf{k}| \) is the wavenumber. As the limit \( \lim_{r \to \infty} g(r) = 1 \), the integral in equation 3.11 diverges. Rewriting equation 3.11 as

\[ S(k) = 1 + \rho \int (g(|r|) - 1) \exp(-i \mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r} + \rho \delta(k), \]  
(3.12)

where \( \delta(k) = \int \exp(-i \mathbf{k} \cdot \mathbf{r}) \, d\mathbf{r} \), we have equation for \( S(k) \) where the first two terms are finite (i.e. the first integral converges). The \( \delta(k) \) term corresponds to the coherent forward scattering from the fluid and is significant only at \( k = 0 \). It is therefore omitted from the definition of \( S(k) \) in terms of the Fourier transform of \( g(r) \) [36].

Thus there are two methods to calculate the structure factor from real space coordinates as obtained from simulations. The first is by summing the real components of the product of \( \rho_k \rho_{-k} \) (i.e. via equation 3.8) as

\[ S(k) = \frac{1}{N} \left( \left[ \sum_i \cos(\mathbf{k} \cdot \mathbf{r}_i) \right]^2 + \left[ \sum_i \sin(\mathbf{k} \cdot \mathbf{r}_i) \right]^2 \right). \]  
(3.13)

The second method calculates the Fourier transform of the radial distribution function.
Figure 3.2: The static structure factor $S(k)$ for the three phases of the LJ model listed in figure 3.1. (a) Gas, (b) liquid, and (c) crystal. Black lines are $S(k)$ calculated directly from the real space coordinates (equation 3.13), and red lines are from the Fourier transform of $g(r)$ (equation 3.14).

(first two terms in equation 3.12) as the integral

$$S(k) = 1 + 4\pi\rho \int_0^\infty r^2 (g(r) - 1) \frac{\sin(kr)}{kr} dr.$$  \hspace{1cm} (3.14)

There are caveats for numerically evaluating $S(k)$ by either of these methods. The choice of wavevector $k$ for evaluating equation 3.13 is restricted by the geometry of the configuration space. For simulations in a cubic box with periodic boundary conditions (PBCs), as employed in this thesis, the wavevectors are quantised as $k = \frac{2\pi}{V^{1/3}} (n_x, n_y, n_z)$ where $n_x, n_y$ and $n_z$ are non-negative integers. In practice only the wavevectors parallel to the sides of the simulation box are used to evaluate $S(k)$ by equation 3.13.

If calculating $S(k)$ from the Fourier transform of $g(r)$ via equation 3.14, the integral to infinity is necessarily truncated at an upper limit equal to the maximum correlation length accessible in the simulation. For a cubic simulation box with periodic boundary conditions this is $V^{1/3}/2$. The effect of the truncation is to introduce unphysical oscillations into $S(k)$ for low $k$. It is possible to use either of these methods on systems that are out of equilibrium, or if translational or rotational invariance is broken.

In figures 3.2(a)-(c) we show structure factors for the gas, liquid and crystal phases of the LJ model. There are only weak peaks in $S(k)$ for the gas (figure (a)) indicating that there is little structuring of the particles. The rise in $S(k)$ at low $k$ indicates that the isothermal compressibility of the gas is large. The noise in the data for $S(k)$ calculated from the coordinates (black line) is due to the quantisation of the wavevectors.

Figure 3.2(b) shows $S(k)$ for a liquid. The large first peak is at $k \approx \frac{2\pi}{r_{\text{peak}}}$, where $r_{\text{peak}}$ is the peak spacing in $g(r)$, and corresponds to scattering off layers of neighbouring particles in the liquid. The wavenumber for the position of the first peak of $S(k)$ in liquids is henceforth denoted by $k_p$. The subsequent peaks for increasing $k$ are at approximately
integer multiples of $k_p$ and also arise due to scattering from adjacent layers of particles in the liquid.

Compared to the gas structure factor, there are fewer wavenumbers sampled when calculating $S(k)$ directly from the coordinates as the simulation box is smaller. The oscillations at low $k$ in the Fourier transform of the radial distribution function (red line) are artefacts that arise due to the finite range accessible for $g(r)$, again due to the finite size of the simulation. These oscillations are unphysical and direct calculation of the structure factor from the coordinates reproduces more faithfully the low-$k$ behaviour of $S(k)$ for the liquid.

Calculations of $S(k)$ for a face-centred cubic crystal are presented in figure 3.2(c). Although the angularly averaged $S(k)$ is technically not well-defined for this phase, we present the data to highlight the following points: The sharp peaks in $S(k)$ arise due to the periodicity in the particle positions on the crystal lattice. The peaks clearly observed with the direct calculation of $S(k)$ from the coordinates (black line) are because the wavenumber $k$ is only angularly averaged over wavevectors parallel to the sides of the simulation box. These directions coincide with in the principle lattice vectors for the crystal (i.e. the Miller indices 100, 010, 001). The Fourier transform of $g(r)$ (red line) is angular averaged in all directions and hence includes numerous peaks and troughs in $S(k)$ due to convolutions of scattering from the crystal lattice.

3.5. The neighbour network

Many of the methods for structure detection rely on determining the nearest neighbouring particles of each particle as an input into their algorithms. There is no single accepted criterion to define what a neighbour of a particle is and there are many ways to do so. The results from each of the algorithms will necessarily depend on how the neighbours were chosen and care is needed when choosing a method to identify the neighbours in order that the results obtained are physically relevant. We term the sets of neighbours for each of particles as the neighbour network.

Two methods are commonly implemented to find the neighbours for each particle. The methods work by either (i) using a cut-off for the maximum separation between neighbouring particles, or (ii) using a Voronoi construction to divide up the system volume into cells containing a single particle and defining the neighbours by the cells that share faces. In this section we review these two methods before discussing a modified Voronoi construction to detect the neighbours that is optimised for the TCC algorithm. However, before we can proceed we need to define some notation to represent the particles and their neighbours in a given system.
3.5.1. Notation for the neighbour network

Formally we define the neighbour network or bond network for a system of particles as an undirected graph $G = (V, E)$. This network contains the information for all the neighbours of each particle in a system. The set $V$ is the $N$ positions of the particles $r^N$, and $E$ is a set of edges that connect two vertices. We refer to the elements of $E$ as the neighbour links or bonds$^4$ between pairs of particles.

A graph $g = (v, e)$ is a subgraph of $G$, written $g \subseteq G$, if all the particles of $v$ are also in $V$, and all the bonds of $e$ are present in $E$. Many of the cluster-derived approaches for identifying structure work by identifying the neighbour network $g$ of a small cluster and solving $g \subseteq G$ to see if that structure exists in the bulk. This is the case for the CNA and the VFA methods discussed in the introduction to this chapter.

The TCC algorithm differs from the CNA and the VFA methods in that it offers a number of candidate networks $g_c$ for a structure to exist in the bulk. The candidate networks have similar structure to the bond network $g$ of a ground state cluster of the interaction potential. Specifically the candidate networks $g_c$ have the same number of vertices and a similar set of bonds as $g$ for the ground state cluster.

The advantage of having multiple bond networks to detect a cluster in a bulk is that it allows the cluster to adopt more thermally distorted configurations and still being identified as the cluster than when there is just a single network $g$ for detection. Using candidate networks can also simplify the coding of the detection routines. This is because using candidate networks may reduce the number of bonds $e$ that must be checked for if two of the candidate networks differ only the existence of a particular bond.

The general problem of finding solutions to $g_c \subseteq G$ is known in theoretical computer science as the subgraph isomorphism problem. The problem belongs to the NP-complete computational complexity class [37] and there is no known algorithm to find solutions in polynomial time of the problem size. However in the setting of finding structures within liquids of simple atomic or colloidal particles, the steric of the interactions between the components and the typical sizes of clusters of interest mean that finding solutions to $g_c \subseteq G$ is usually computationally tractable.

The network distance $d_G(i, j)$ between any two particles in $G$ denoted by indices $i$ and $j$ is the minimum number of bonds that must be traversed through the network in order to connect the particles. The first-nearest neighbours of a particle have $d_G = 1$, the second-nearest neighbours have $d_G = 2$, and so forth.

$^4$The term bond is not used in a strict chemical sense, i.e. that some attractive interaction binds two particles together, but instead just to denote that two particles are considered as neighbouring each other. For systems with purely repulsive interactions, such as hard spheres, particles can be said to be bonded, i.e. neighbours, even in the absence of an attractive interaction.
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Figure 3.3: (a) The bond length criterion for identifying neighbours. Particles \( i \) and \( j \) are bonded as \( r_{ij} < r_c \). (b) A Voronoi tessellation in two dimensions. The cell around the central particle contains all the points in space that are closer to it than any of the other particles. (c) A Voronoi tessellation of a system of spheres in 3D found using the Voro++ package \[38\]. The particles are coloured according to the number of faces of their Voronoi cell.

3.5.2. Detecting neighbours using a bond length cut-off

The simplest way to identify the neighbours of each particle is to define a maximum length for the bonds. The cut-off length is denoted by \( r_c \) \(^5\) and all pairs of particles separated by distances less than \( r_c \) are said to be neighbours (figure 3.3(a)). Converesely pairs with separations greater than \( r_c \) are not bonded.

This method uses a single parameter method to determine the bond network. The length \( r_c \) is conventionally taken to be the position of the first minimum in the radial distribution function \( g(r_{\text{min}}) \). This yields \( n_b \) neighbours for each particle, where \( n_b \) is the coordination number of the particle (see section 3.6.2).

For binary systems it is common to use the positions of the first minima in the partial radial distribution functions \( g_{AA}(r) \), \( g_{AB}(r) \) and \( g_{BB}(r) \) to yield three cut-off lengths \( r_c^{AA} \), \( r_c^{AB} \) and \( r_c^{BB} \) to determining the neighbours, dependent on the species of the pair.

The simple bond method is well-suited for use on systems with short-range and sticky interactions \([31, 39]\), as the first minimum in radial distribution function will be close to 0 in the condensed phases. The cut-off length \( r_c = r_{\text{min}} \) provides a robust boundary for separating the first and second nearest neighbours of a particle. The resulting neighbour network will show little sensitivity to small changes to \( r_c \) if it remains close to \( r_{\text{min}} \).

For many liquids, glasses, and crystals with complicated unit cells or large thermal fluctuations of the particles about the lattice sites, the first minimum of \( g(r) \) is not close to zero. This means that there is not a well defined length that separates first and second

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\(^5\)The cut-off length for identifying neighbours should not to be confused with the truncation length for the potential, which is frequently denoted as \( r_c \) in the literature. In this thesis \( n_t \) is the truncation length of a potential, and \( r_c \) is the cut-off length for determining the neighbours.
nearest neighbours. The results obtained from any structure detection algorithm will be sensitive to the choice of $r_c$, as the number of bonds in the bond network may vary appreciably for small changes to its value.

To further clarify this problem it is insightful to consider four particles located at the vertices of a square with sides $r$. The separation between particles on opposite sides of the square is $\sqrt{2}r$. For the LJ liquid studied in figure 3.1(b), the position of the first minimum of $g(r)$ is $r_{\text{min}} = 1.54$. This is greater than $\sqrt{2}r_{\text{peak}} = 1.50$, where $r_{\text{peak}}$ is the position of the first peak in $g(r)$ and an estimate for the mean particle separation. Any structures based on the integrity of four-fold symmetric ring of particles, as for a square, may go undetected if particles at opposite vertices are erroneously detected as nearest neighbours.

Another issue with using $r_c = r_{\text{min}}$ is that $r_{\text{min}}$ is a state point dependent quantity and adjustments may be necessary to account for drift in $r_{\text{min}}$ when analysing different state points. In practice the value of $r_{\text{min}}$ only varies weakly with state variables for the regions of phase space of the systems that are considered in this thesis.

Using a single value for $r_c$ can present problems when studying phase transitions at a single state point [40]. Crystallisation free-energy barriers and rates are calculated using umbrella sampling techniques with a structure detection method acting as a reaction coordinate [25, 41, 42]. The position of the first minimum of $g(r)$ reduces when going from the liquid to the crystal phase as the particles become localised to the lattice sites. This means that a single value of $r_c$ may not be appropriate for characterising the structure in both the liquid and solid phases while a transition is ongoing. Changes in bond ordering during nucleation are more clearly seen using a method for neighbour detection that is not sensitive to a range parameter, such as taking the nearest $n$ particles to be the neighbours [43].

In summary, identifying the neighbours using a maximum separation criterion works well for systems with clear distinctions between the first and second nearest neighbours, indicated by a deep first minimum of $g(r)$. Such systems include those with strong short-range attractions and low temperature crystals. For other systems care must taken when choosing the value of $r_c$, as the value of the first minimum of $g(r)$ depends both on the state point and the locality in space if any phase transitions are occurring or interfaces are present. If the first minimum of $g(r)$ is not close to zero, any small adjustments to $r_c$ and hence the number of detected bonds will result in changes to the structural order parameters that are detected.

3.5.3. Detecting neighbours with Voronoi tessellations

Although simple and intuitive the main disadvantage of using a cut-off length to determine a particle’s neighbours is the sensitivity of the result to the chosen length and
the consequences this may have for the structure detection algorithm. A method that can identify the neighbour network independently of an adjustable length parameter is therefore appealing. One such method where this property holds is the Voronoi method.

In the Voronoi method, a Voronoi tessellation decomposes space into regions of non-intersecting domains with distinct boundaries [44]. Each region contains the position of a single particle and all points in space closer to that particle than any other. In three dimensions these regions are convex polyhedra that are termed Voronoi cells. In solid state physics the Voronoi cell is more commonly known as the Wigner-Seitz cell.

An example of a Voronoi tessellation is shown in figure 3.3(b) for a 2D system and in three dimensions in figure 3.3(c). Particles are said to be neighbouring if their Voronoi cells share a face. This defines the neighbour network independently of any adjustable parameters.

Two particles with Voronoi polyhedra that share only an edge or a vertex are not considered bonded. It is important to make this clear as later on we will consider the detection of four-fold rings of particles with the Voronoi method. In practice fluctuations of the particle positions in thermal systems mean that edge- and vertex-sharing polyhedra are rare.

The properties of Voronoi cells for disordered systems were first studied in [2–4] and subsequently the method of using a Voronoi tessellation to define neighbour a network was popularised in studies of crystallisation [6] and glass-formers [45].

The early studies of crystallisation noted that the detection of the crystal-order when using the Voronoi method was highly sensitive to thermal fluctuations of the particle positions [6, 13, 15]. The Voronoi cell of a particle in a $T = 0$ FCC crystal contains six vertices that are each common to four faces. Small thermal vibrations lead to these vertices being split into two vertices joined by a new edge. This adds a new common face between two of the Voronoi cells of the neighbouring particles, and consequently adds a new bond to the system. The additional bond complicates the detection of the crystalline order.

This problem is equivalent to the unwanted bond forming across a square of particles as discussed in the previous section. Poor performance is often found when trying to detect structures with four-fold symmetries (e.g. octahedral structures) in structure detection methods using the Voronoi neighbour network. For this reason numerous authors have proposed modifications to the Voronoi method in order that the detected bond network is more robust to thermal fluctuations of the particles [13, 14, 46–48].

The sensitivity of the Voronoi method to thermal fluctuations can be demonstrated by examining the number of first-nearest neighbours it detects for FCC and HCP crystals. Frequently second-nearest neighbours are misdetected as first-nearest neighbours [14, 48, 49], meaning that the number of the first-nearest neighbours is inflated [50].
Williams proposed a modification for the Voronoi method when introducing the TCC structure algorithm to address this issue [34]. The method adds a dimensionless parameter that sets the maximum amount of distortion that a four-membered ring in a plane can undergo before a bond forms between particles at opposite vertices. Good performance was found for detection of octahedral structures in the hard sphere liquid [34] and it is found here that detection of FCC and HCP order is improved using the modified Voronoi bond detection method.

The Voronoi method is attractive in that the neighbour network can be identified without having to select an adjustable parameter. It provides a natural and intuitive way to determine the neighbours for each particle. The method has problems when thermal vibrations destroy degenerate vertices and this scenario is especially relevant for the detection of crystalline order if the number of first-nearest neighbours for each particle is over-estimated.

3.5.4. A modified Voronoi method

The Williams modified Voronoi method makes two modifications to the original Voronoi method (hereafter referred to as the standard Voronoi method). The modifications are introduced to improve the detection of the four- and five-membered rings of particles [34].

The first modification ensures that particles are neighbours if and only if their Voronoi cells share a face and the line that connects the particle positions also intersects the shared face. This condition is depicted in figure 3.4 for a 2D system. Such neighbouring pairs are the direct Voronoi neighbours introduced by Meijering [51–53]. Connections between direct neighbours are highlighted in figure 3.4(a) with blue lines.

Employing only direct neighbours has two effects on the neighbour network when compared to the standard Voronoi method:

1. It strictly reduces the number of bonds derived from the Voronoi tessellation. The removed bonds occur when the volume of the Voronoi cell of a third particle overlaps with the line connecting the positions of two particles that share a Voronoi face. The third particle shields the pair and a bond present in the standard Voronoi method is removed (figure 3.4). The removed bonds are ‘long bonds’ that cause misdetection of second-nearest neighbours as first-nearest neighbours.

2. Algorithms to detect direct neighbours are generally simpler to implement than those to find all Voronoi neighbours.

The direct neighbours of particle $i$ are identified by first finding all particles within some cut-off distance $r_c$, which can be made as large as required. These particles are ordered in increasing distance from $i$. A particle $k$ is a direct neighbour of $i$ if for all $j$
Figure 3.4: The first modification to the standard Voronoi method is to consider only the direct neighbours. (a) The lines that connect particle centres must also intersect the face that is shared between the two Voronoi cells for the particles to be bonded. Particles $i$ and $j$ are not bonded therefore, as highlighted by the red line connecting their positions. Conversely all other particles are considered neighbours of particle $i$ (blue lines - direct neighbours). Particle $k$ is closer to $i$ than $j$, and the volume of its Voronoi cell is shielding particle $j$ from particle $i$. (b) and (c) Identification of direct Voronoi neighbours. Particle $k$ is further from $i$ than $j$ in both cases. In (b) particle $k$ is not bonded to $i$ as there exists $j$ that is closer to $i$ and the angle subtended by vectors $r_{ij}$ and $r_{kj}$ is greater than $\pi/2$ radians. Conversely $k$ is bonded to $i$ in (c) as the bond there is no shielding by $j$. 
Figure 3.5: Detection of four-membered rings of particles. (a) Particles are positioned at the vertices of a rhombus. In the case that $h = w$, i.e. a square, there is no bond between particles $i$ and $k$. If $h < w$ then a bond forms between $i$ and $k$ across the rhombus if using the standard Voronoi method. (b) The detection of an octahedral cluster with the CNA and TCC methods relies on the integrity of its four-membered rings, e.g. the ring highlighted in red. Thermal fluctuations cause this structure to be detected incorrectly with these methods if using the standard Voronoi algorithm to determine the neighbour network.

Closer to $i$ than $k$ is the angle subtended by the vectors $r_{ij}$ and $r_{kj}$ is less than $\pi/2$ radians. Or equivalently the inequality

$$r_{ij} \cdot r_{kj} > 0,$$  \hspace{1cm} (3.15)

holds $\forall j$, where $|r_{ij}| < |r_{ik}|$. Figures 3.4(b) and (c) show cases where this condition is not and is satisfied respectively.

The second modification to the standard Voronoi method improves detection of four-membered rings of particles. Consider particles placed at the vertices of a rhombus, as in figure 3.5(a). If the rhombus were a perfect square there would be a total of four bonds detected by the standard Voronoi method, each running along the edges of the square. If the square is distorted to form a rhombus a bond forms between two particles on opposite vertices, thus creating two three-membered rings of particles. This bond breaks the detection of any cluster based on the integrity of a four-membered ring, e.g. the octahedral cluster shown in figure 3.5(b), when any small fluctuation distorts the ring in the plane.

A dimensionless parameter $f_c$, known as the four-membered ring parameter [54], is introduced that determines the maximum amount of asymmetry of a four-membered ring of particles before it is identified as two three-membered rings. Bonds between particles $i$ and $k$ will be removed if there exists a particle $j$ that is both bonded to $i$ and closer to $i$ than $k$ is, and that shields any bond between $i$ and $k$.

We consider the plane perpendicular to $r_{ij}$ that contains a point $r_p = r_i + f_c(r_j - r_i)$. If $f_c < 1$ this corresponds to moving the plane perpendicular to $r_{ij}$ and containing $r_j$. 


towards $r_i$ (figure 3.4(c)). Adapting equation 3.15, the condition for $k$ to be bonded to $i$ is bonded if $\forall j$ where $|r_{ij}| < |r_{ik}|$:

$$r_{ip} \cdot r_{kp} > 0, \quad (3.16)$$

Expanded in $j$ ($f_c \neq 0$)

$$f_c(r_i \cdot r_j + r_j \cdot r_j - 2r_i \cdot r_j) > r_i \cdot r_i + r_j \cdot r_k - r_i \cdot r_j - r_i \cdot r_k. \quad (3.17)$$

Equation 3.17 is not invariant to swapping indices $i$ and $k$. The consequence of this is that $i$ may be bonded to $k$ but not vice versa. It is therefore necessary to consider bonding from the point of view of particle $k$. The plane perpendicular to $r_{kj}$ containing $r_j$ is moved towards $k$ such that it contains the point $r_q = r_k + f_c(r_j - r_k)$. From the viewpoint of particle $k$, particles $i$ and $k$ are neighbours if $\forall j$ where $|r_{kj}| < |r_{ik}|$:

$$r_{kq} \cdot r_{iq} > 0. \quad (3.18)$$

The inequalities of equations 3.16 and 3.18 are depicted geometrically in figures 3.6(a) and (b). Both inequalities are not satisfied as the angles $\theta$ are obtuse.

Adding together equations 3.16 and 3.18 yields a single, symmetric, criterion for $i$ and $k$ to be bonded. If $\forall j$ with $|r_{ij}| < |r_{ik}|$

$$r_{ip} \cdot r_{kp} + r_{kq} \cdot r_{iq} > 0, \quad (3.19)$$
Figure 3.7: Criterion to determine four-membered and three-membered rings. For a given rhombus defined by \( h/w \) or \( \theta \), the existence of the bond between \( i \) and \( k \) depends on the value of \( f_c \).

\( i \) and \( k \) are said to be neighbours. Equation 3.19 is invariant to inversion of the indices \( i \) and \( k \), therefore the resulting neighbour network is necessarily symmetric. A symmetric bond network is required in order to use either the CNA or TCC algorithms to identify structure. Expanding equation 3.19 in \( j \) and setting \( f_c = 1 \) recovers the criterion for the direct neighbours of the standard Voronoi method (equation 3.15).

To demonstrate the effect of \( f_c \) we reconsider the rhombus of particles in figure 3.5(a). The parameter \( f_c \) determines the maximum asymmetry of the rhombus \( (h/w) \) before a bond forms between particles \( i \) and \( k \) on opposite vertices (figure 3.7). Expanding and rearranging equation 3.19 gives an inequality for a bond to exist between \( i \) and \( k \) in terms of the particle separations:

\[
f_c > \frac{r_{ik}^2}{r_{ij}^2 + r_{jk}^2}.
\]  

(3.20)

Using \( r_{ij} = r_{jk} \) (side lengths of a rhombus are equal), \( r_{ik} = h \) and Pythagoras’ theorem gives this condition in terms of the lengths \( h \) and \( w \):

\[
f_c > \frac{2}{1 + (w/h)^2}.
\]  

(3.21)

If \( f_c \) is greater than this value then there is a bond between \( i \) and \( k \) and the rhombus of particles is identified as two three-membered rings. Conversely if \( f_c \) is less than or equal to this value then \( i \) and \( k \) are not bonded and the rhombus may be a four-membered ring subject the status of \( j \) and \( l \). This is found by swapping \( w \) and \( h \) in equation 3.21.

In terms of the angle \( \theta \) subtended by the bonds connecting \( j \) to \( i \) and \( k \), the condition
for $i$ and $k$ to be bonded is

$$f_c > \frac{2}{1 + [\tan(\theta/2)]^{-2}}. \quad (3.22)$$

For angles less than $\theta$, $i$ and $k$ are bonded. If $f_c = 1$, the angle $\theta = \pi/2$ and for $f_c = 0.82$ we have $\theta \approx 1.39 \approx 80^\circ$.

The limit for validity of equation 3.22 is $\theta \leq \pi/3 \leq 60^\circ$, i.e. valid choices for $f_c$ are in the range $(0.5, 1]$.

### 3.5.5. Algorithm for the modified Voronoi method

Here we describe an algorithm to identify the modified Voronoi neighbour network:

1. Loop over all $N$ particles with index $i$.

2. Find all particles within $r_c$ of $r_i$, where $r_c$ is to be longer than the longest bond in the network, and add to a set $S_i$. The speed of this step can be improved by using a cell list (chapter 2).

3. Order the particles in $S_i$ by increasing distance from particle $r_i$.

4. Loop over all elements $j$ in $S_i$, i.e. particles in increasing distance from particle $i$.

5. For each $j$ loop over all $k > j$ in $S_i$ and eliminate $k^{th}$ particle from $S_i$ if inequality 3.20 is not satisfied.

The particles left in the sets $S_i$ on completion are the neighbours of particle $i$. The algorithm is depicted in the flow diagram in figure 3.8.

The value of $r_c$ can be used to set the maximum bond length in the system. Doing so would be useful if studying gels or cluster fluids, for example, where long bonds are not desired between gaseous particles or particles in separate clusters.

### 3.5.6. Comparison of the neighbour detection methods

We compare the neighbour detection methods by considering a LJ system at fixed temperature $T = 0.92$ and pressure $P = 5.68$ as studied by ten Wolde et al. [25]. The simulations are Monte Carlo (MC) in the constant $NPT$ ensemble and the potential is truncated at $r_{tr} = 2.5$. This state point corresponds to roughly 20% undercooling of the liquid phase [25].

Four phases are considered: a supercooled liquid with $N = 864$, a FCC crystal with $N = 864$, a HCP crystal with $N = 1000$ and a body-centred cubic (BCC) crystal $N = 1024$. The supercooled liquid is initialised by random insertion with $r_{ol} = 0.9$, and the crystals by particles on the lattice sites of a crystal filling the simulation box. These samples are
Figure 3.8: Algorithm for detecting neighbours using the modified Voronoi method. The apostrophes on \( j \) and \( k \) indicate the particles referenced by the \( j^{th} \) and \( k^{th} \) elements of the set \( S_i \).
Figure 3.9: (a) The radial distribution functions for four phases of a LJ system at state point $T = 0.92$ and $P = 5.68$. Note that the position of the first minima of $g(r)$ for the FCC and HCP phases is different from that of the BCC and liquid phases. A single cut-off length cannot determine the neighbours consistently across all the phases. (b) Frequency of bond lengths for different neighbour detection routines. The simple cut-off method is the dotted line ($r_c = 1.4$) and it drops vertically to zero frequency upon the maximum bond length. The standard Voronoi method is the black line [38] and the coloured lines are for the modified Voronoi method. The effect of reducing $f_c$ is to remove neighbour pairs that have large separations (long bonds) from the standard Voronoi neighbours.

used to assess the performance of the structure methods described later in this chapter, but first we compare the cut-off, standard and modified Voronoi bond detection methods.

In figure 3.9(a) the radial distribution function for each phase is plotted about the first minimum. The position of the first minimum is different for the liquid and BCC phases, $r_{min} \approx 1.5$, is different from that of the FCC and HCP crystal phases, $r_{min} \approx 1.36$. A single cut-off length does not therefore determine the neighbours consistently between the phases with respect to $r_{min}$. This may cause problems if interfaces exist in the system, or if nucleation and growth is occurring [40].

In figure 3.9(b) we plot the distribution of bond lengths between neighbours for the under-cooled liquid as identified by the different detection methods. If all particles were neighbours the distribution of bond lengths is an unnormalised plot of $4\pi\rho r^2 g(r)$. All the data coincide up to the first peak indicating that these neighbours are detected by all the different methods for bond detection.

The data for the simple cut-off method drop abruptly to zero at the cut-off length $r_c = 1.4$, whereas the Voronoi methods show a smooth transition to zero. The standard Voronoi method gives the largest number of neighbours in total and includes a number of pairs with separations greater than $r_{min} = 1.5$ for this phase.

The effect of only considering direct neighbours as bonded with the modified Voronoi method is clear when comparing the $f_c = 1.0$ data to that of the standard Voronoi method.
The difference between the graphs indicates that the indirect neighbours have relatively long bonds.

The effect of reducing $f_c$ is to further reduce the number of neighbours with longer separations. The ideal choice for $f_c$ will be a function of the structure detection method that is being utilised. Typically cluster detection algorithms, such as the TCC, are sensitive to the inclusion of ‘long bonds’ as these may cause misdetection of structures. BOO parameters on the other hand are less sensitive to the inclusion of long bonds providing second nearest neighbours are not included.

Williams proposed a suitable value $f_c = 0.82$ for the TCC method based on a study of the hard sphere fluid [34]. We also take this value except where explicitly stated otherwise. The choice for $f_c$ is discussed further in the sections below.

### 3.6. Established measures of quantifying the structure

In this section we review a number of structure detection methods for particulate systems. All of the methods employ a neighbour network in order to detect structure, although the method of the VFA algorithm is not usually described in this way. For each of the structure detection algorithms any method can be used to detect the neighbour network, with the notable exception of the largest standard cluster analysis (LSCA) method that generates a neighbour network actively during the running of its algorithm.

#### 3.6.1. Bond-angle distributions

Bond-angle distributions are a three-body measure based on the angle subtended between a particle and the directions to two of its neighbours. For a particle $i$ and a pair of its neighbours $j$ and $k$, this angle is given by

$$\cos(\theta) = \frac{\mathbf{r}_{ij} \cdot \mathbf{r}_{ik}}{|\mathbf{r}_{ij}| |\mathbf{r}_{ik}|}, \quad (3.23)$$

see figure 3.10(a).

Averaging the bond angles of all neighbouring triplets yields a distribution that can be used to characterise the local structure in a system. This distribution shows significant changes during ordering transitions such as when a liquid crystallises, see figure 3.10(b), [13, 15, 55]. It also has been used to demonstrate structural differences between models for liquids with attractive interactions and their purely repulsive counterparts [16], and between heterogeneous environments in supercooled liquids [11].
Figure 3.10: (a) The bond-angle $\theta$ between the neighbours $j$ and $k$ of central particle $i$. (b) Change in bond-angle distributions in simulations of rubidium from the liquid (top panel) to the predominantly BCC crystal phase (bottom panel). The sharp peaks correspond to the local orientation of each particle’s neighbours on the lattice sites. Figure adapted from [55].

3.6.2. The coordination number

The coordination number $n_b$ is the number of nearest neighbours a particle has. The average coordination number for a system is usually defined by the integral of $r^2 g(r)$ up to the first minimum of $g(r)$:

$$ \bar{n}_b = \int_0^{r_{\min}} 4\pi r^2 \rho g(r) \, dr. $$

An alternative definition defines the coordination number as the mean number of neighbours each particle has in a given neighbour network. Coordination numbers are typically quoted in crystallography where particles in athermal FCC and HCP crystals both have $\bar{n}_b = 12$ and particles in BCC crystals have a coordination number of 8.

Distributions of coordination numbers can be used to measure the variation in structure within disordered systems [2]. The individual coordination number of a particle is correlated with its dynamical behaviour in certain systems. For instance, a strong correlation is seen between these quantities in gels [31].

In figure 3.11 the average coordination number calculated from modified Voronoi bond networks is plotted for the LJ phases as a function of $f_c$. Lowering $f_c$ reduces the coordination number. For comparison the coordination numbers obtained from the cut-off
Figure 3.11: The effect of the $f_c$ parameter on the average coordination number $\bar{n}_b$. The red line for FCC crystal is obscured by the green line for the HCP phase.

Table 3.1: The average coordination number $\bar{n}_b$ for different bond detection methods. The first minimum of $g(r)$ is $r_{\text{min}} \approx 1.5$ for the liquid and BCC phases, and $r_{\text{min}} \approx 1.36$ for the FCC and HCP phases.
and standard Voronoi methods are displayed in table 3.1. The standard Voronoi method gives rather large coordination numbers $\approx 14$ for all the phases at this state point.

The cut-off method gives 12 nearest neighbours for the FCC and HCP phases when choosing $r_c$ as the first minimum in $g(r)$ for these phases. This yields value of $\bar{n}_b = 11.1$ for the liquid, lower than $\bar{n}_b = 13.0$ that arises when the cut-off is the first minimum of the liquid $g(r)$. The modified Voronoi method with $f_c = 0.82$ reproduces the correct coordination number of the FCC and HCP crystals and gives a coordination number of $\bar{n}_b = 11.1$ for the liquid.

All the bond methods overestimate the coordination number for the BCC phase. This is because thermal fluctuations smear out the small maximum in $g(r)$ that occurs between the first and second nearest neighbours in the crystal structure. A BCC crystal is not a close packed structure, and the small difference between the relative distances to the second and first minima (the ratio of these distances is 1.15) makes the first nearest neighbours difficult to detect without dilution of second nearest neighbours. This consequently means that it is challenging to detect BCC ordering using cluster-based structural identification algorithms.

### 3.6.3. Common-neighbour analysis

The common neighbour analysis (CNA) was introduced by Honeycutt and Andersen to analyse the structural changes that occur in the melting and freezing of LJ clusters [5]. It is a cluster-based approach that focuses on the particles that are neighbours of both particles in a pair. Each pair of particles that share some neighbours are termed a root pair and they need not be bonded themselves (although they frequently are for clusters of interest).

Four integers are used to define each type of cluster uniquely. The first integer is either 1 if the root pair are bonded or 2 if otherwise. The second indicates the number of particles that are neighbours of both the root pair particles - these are the common neighbours. The third integer counts the number of bonds between the common neighbours. The fourth index is used to separate clusters where the first three indices are degenerate and needs to be defined with reference to a diagrammatical key. Figure 3.12 contains some examples of CNA clusters where the root pair is not shown and the bonds between the common neighbours (black circles) are shown by solid lines.

The common-neighbour analysis has been modified and extended in a number ways. The fourth index is frequently substituted as the number of bonds in the longest continuous chain of bonds between the neighbours [56]. Both Lümmen and Kraska [57] and Pedersen [58] proposed extensions for binary mixtures. A method called the cluster bond-type index method (CBTIM) was developed to describe the structure of the coordination shell in terms of CNA pairs [59, 60]. CBTIM analysis yields four indices for
Figure 3.12: Common neighbour analysis diagrams indicating the clusters that are frequently seen in dense atomic systems. Black circles denote common neighbours and black lines the bonds between them. The pair of particles that share the common neighbours are not themselves shown. Figure adapted from [5].
3.6.4. Voronoi face analysis

The Voronoi face analysis (VFA) traces its origins back to early papers by Bernal [2] and Rahman [3], and was later formalised by Finney [4] and Tanemura et al. [6]. They noted that for dense systems such as liquids, glasses and solids, the Voronoi cell for a particle can be described in terms of the number of edges on each face. Each polyhedron is given an index formed as a set of integers \((n_3, n_4, n_5, \ldots)\), where \(n_i\) is the number of faces with \(i\) edges. This index describes the structural arrangement of the neighbours in a particle’s coordination shell.

The Voronoi polyhedra for particles in face-centred cubic and body-centred cubic environments are shown in figure 3.13. For example, the FCC polyhedron has twelve faces with four sides so its VFA index is \((0, 12)\). Correspondingly the BCC polyhedron is denoted \((0, 6, 0, 8)\) due to its six four-fold faces and eight six-sided faces.

The Voronoi polyhedron of an HCP particle also has a VFA index of \((0, 12)\), i.e. identical to FCC. This indicates that the structure ascribed by a VFA index is not necessarily unique. The number of connections between vertices around a face can be considered in order to distinguish between FCC and HCP crystal ordering if using the VFA analysis [14].

In the appendix of [6] it is noted that the degeneracies of the vertices of faces in a FCC Voronoi polyhedron mean that detection of \((0, 12)\) is easily broken when the system is thermal. In data obtained from either simulations or experiments degenerate vertices...
are rare if using the standard Voronoi method to detect the bonds. The consequence of this is that (0,12) polyhedra are rarely identified.

Tanemura et al. employed equilibrium simulations of FCC and HCP crystals to identify the Voronoi polyhedra that are formed when the crystals are subject to thermal excitation. Structural changes during crystallisation events were then compared to these inferred VFA indices for crystalline order [6].

Although the VFA algorithm is defined without reliance on a neighbour network as an input, it is possible to define the method with equivalent results in terms of a neighbour network. Assuming that there are no degenerate edges or vertices in the Voronoi tessellation, i.e. edges or vertices that are shared between four or more Voronoi polyhedra, then the number of edges on the face of a Voronoi polyhedron for particle \( i \) that is common with a face for particle \( j \) corresponds to the number of bonds that \( j \) has to other particles in the coordination shell of \( i \). This means the VFA indices for a particle can be calculated by counting the bonds between from each particle in the coordination shell to others in the coordination shell.

As discussed in section 3.5.3, a number of modifications have been proposed to detection Voronoi neighbours. The proposed modifications include merging two vertices if the distance between them along an edge is smaller than a threshold value [13, 14], removing faces with small areas [61], or both [46, 62]. Authors have also proposed parameter-free modifications [47, 48].
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3.6.5. Planar graph analysis

Planar graph analysis is another method that detects clusters in bulk systems. It bears many similarities to the VFA method. The local structure around a central particle is characterised in terms of the bonds between its neighbours. The neighbours and their bonds are represented respectively by vertices and edges in a two-dimensional planar graph [48, 63]. The planar graph is characterised in terms of the number of primitive rings it contains and their arrangements around a vertex [48, 63]. This is useful for distinguishing between FCC and HCP crystal structures [48].

The advantage of the planar graph method is that any fluctuations of bonds between the neighbours are more easily visualised on the planar graph than in 3D space [48]. This method has been used to study crystal melting [63], metals under shear [63], and crystallisation of gold nanoclusters [64].

3.6.6. Bond orientational order parameters

A complementary stand of structural order parameters has been developed in parallel to the cluster algorithms discussed above. Bond orientational order (BOO) parameters quantify the correlation of the bonding around a particle to the spherical harmonic solutions of Laplace’s equation [17, 18]. The BOO parameters describe a continuous change in structure, unlike the cluster methods which determine whether the order exists or not in a binary fashion.

The spherical harmonics $Y_{lm}(\theta(\mathbf{r}), \phi(\mathbf{r}))$ are complex numbers that form the angular portion for the solutions to $\nabla^2 f = 0$. They are an orthonormal basis for the Hilbert space of square integrable functions $f$. The angles $\theta(\mathbf{r})$ and $\phi(\mathbf{r})$ are the polar angles of a vector $\mathbf{r}$ with respect to a reference coordinate system. The number $l$ is a non-negative integer.
and \( m \) is an integer within the bounds of \([-l, l]\). For even and zero \( l \) \( Y_{lm} \) is invariant to the inversion of the direction of \( r \), meaning that only these values are considered. The spherical harmonics for various \( l, m \) are depicted in figure 3.15.

The complex number \( q_{lm}(i) \) for particle \( i \) is defined as

\[
q_{lm}(i) = \frac{1}{n_{b}(i)} \sum_{j} Y_{lm}(r_{ij}),
\]

(3.25)

where the sum is restricted to the \( n_{b}(i) \) particles \( j \) that are neighbours of \( i \) and the vector \( r_{ij} = r_{j} - r_{i} \) is the direction of the bonds.

The parameter \( q_{lm}(i) \) is sensitive to the choice of reference coordinate system, therefore only rotationally invariant quantities are used as BOO order parameters. The first quantities considered are the local BOO parameters \( q_{l} \):

\[
q_{l}(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^{l} |q_{lm}(i)|^2}.
\]

(3.26)

These quantities are rotationally invariant and independent of the direction of bonds for even \( l \). The values of \( q_{l} \) are strictly non-negative as only the real component from equation 3.26 is utilised.

A second set of order parameters are the third-order invariants:

\[
w_{l}(i) = \sum_{m_{1}+m_{2}+m_{3}=0} \left( \begin{array}{ccc} l & l & l \\ m_{1} & m_{2} & m_{3} \end{array} \right) q_{lm_{1}}(i)q_{lm_{2}}(i)q_{lm_{3}}(i) \left[ \sum_{m=-l}^{l} |q_{lm}(i)|^2 \right]^{3/2}.
\]

(3.27)

The bracketed term is the Wigner 3-j symbol \([66]\) and \( m_{1}, m_{2} \) and \( m_{3} \) are integers between \(-l\) and \( l \) inclusive. The \( w_{l}(i) \) parameters are rotationally invariant for even \( l \) and again only the real components are considered.

The order parameters for a system are interpreted by comparing \( q_{l} \) and \( w_{l} \) with the invariants calculated for known structures. In figure 3.16 \( q_{l} \) and \( w_{l} \) values are shown for structures in a LJ liquid near the melting temperature. The order of a system is determined either locally, i.e. using \( q_{l}(i) \) and \( w_{l}(i) \), or globally as system-wide averages \( \langle q_{l} \rangle \) and \( \langle w_{l} \rangle \).

It was noted that the BOO parameters for particles obtained from simulations of liquids and crystals at fixed temperature and pressure show a large degree of overlap due to thermal fluctuations of the particles. This effect is easily seen in BOO maps like figure 3.17(a), where the distributions of \( q_{6} - q_{4} \) overlap between different phases. This makes it difficult to identify the structure around a single particle with confidence.

Lechner and Dellago proposed a modification to the Steinhardt BOO parameters to
Figure 3.16: BOO parameters $q_l$ and $w_l$ for known structures in a LJ liquid near the melting temperature. The clusters are 13-particle (a) icosahedra, (b) FCC and (c) HCP crystals, as well as (d) 15-particle BCC and (e) 7-particle simple cubic (SC) crystals. Graph reproduced from [18].
tackle this issue. They proposed spatially averaged BOO parameters that consider the ordering of the bonds emanating from a particle and from its neighbours. The spatially averaged counter-parts to the $q_l$ parameters are

$$
\tilde{q}_{lm}(i) = \frac{1}{n_b(i) + 1} \sum_k q_{lm}(k),
$$

(3.29)

The sum here extends over $k = i$ and all of the $n_b(i)$ neighbours of $i$, so that the order parameter is a function of a particle’s first- and second-nearest neighbours. The third-order spatially averaged invariant is

$$
\tilde{w}_l(i) = \frac{\sum_{m_1+m_2+m_3=0} \left( \begin{array}{ccc} l & l & l \\ m_1 & m_2 & m_3 \end{array} \right) \tilde{q}_{lm_1}(i)\tilde{q}_{lm_2}(i)\tilde{q}_{lm_3}(i)}{\left[ \sum_{m=-l}^{l} \tilde{q}_{lm}(i) \right]^{3/2}}.
$$

(3.30)

An averaged BOO map in the $\tilde{q}_6 - \tilde{q}_4$ plane is shown in figure 3.17(b). The distributions of these spatially averaged order parameters show less overlap between the phases than the standard order parameters, allowing more confident discrimination of the local structure around a particle. Any remaining overlaps, such as between $\tilde{q}_6 - \tilde{q}_4$ for the BOO and HCP, can be distinguished by examining other planes, such as $\tilde{w}_4 - \tilde{q}_4$ [67] and $\tilde{w}_6 - \tilde{q}_4$ [43].

It is worth emphasising that the spatially averaged bond order parameters utilise

Figure 3.17: BOO parameter maps for the four phases of a LJ system, $T = 0.92$, $P = 5.68$, defined in section 3.5.6. (a) In the $q_4 - q_6$ plane, (b) in the $\tilde{q}_4 - \tilde{q}_6$ plane. The spatially averaged order parameters differentiates between the local order of the particles in each phase more clearly than the non-spatially averaged BOO parameters.
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Figure 3.18: Spatially averaged BOO parameter maps where the neighbours are calculated using (a) a Voronoi construction [38], (b) the modified Voronoi construction with $f_c = 0.82$. Second nearest neighbours are included in the calculation of $q_{lm}$ when using the standard Voronoi method and this means the separation between the order parameters for each phase is lost. Conversely the modified Voronoi method with $f_c = 0.82$ reproduces a result similar to that of the simple bond method (figure 3.17(b)) independently of any length scale to define the neighbours.

In figure 3.18 the $\tilde{q}_6 - \tilde{q}_4$ BOO maps are shown using Voronoi methods to determine the neighbour network. For the standard Voronoi method (figure 3.18(a)) there is a high degree of overlap between the scatter plots of the order parameters for different phases. This is because the standard Voronoi method overestimates the number of neighbours for the particles, and the calculation of the BOO invariants are dilute by these second near-neighbours.

Conversely the modified Voronoi method with four-membered ring parameter $f_c = 0.82$ (figure 3.18(b)) reproduces the result found using the simple bond method (figure 3.17(b)) and independently of any lengthscale to determine the neighbours.

BOO parameters have been used to study a wide range of systems. Steinhardt et al. searched for icosahedral order within supercooled liquids [17, 18], proceeded by Tomida and Egami [20]. Chakravarty calculated BOO invariants for atomic clusters to discriminate between clusters of different geometry [24]. A popular and active field of research is that of crystallisation, and there many studies using BOO parameters as a reaction coordinate for crystallisation [25, 28, 41–43, 68].

Finally Tanaka has proposed a theory for liquid-glass and liquid-liquid transitions
based on two order parameters: density $\rho$ and bond-orientational ordering described by a BOO parameter [69].

### 3.6.7. The characteristic crystallographic element norm

The characteristic crystallographic element (CCE) norm was introduced to quantify the degree to which the structural ordering around a particle is both orientationally and radially similar to a predefined reference structure [70, 71]. This distinguishes it from BOO parameters that only probe the orientational deviations from the order specified by the spherical harmonic degree $l$. The CCE method is similar to BOO parameters in that it quantifies the correlation with a reference structure using a continuous variable $\epsilon$.

Initially CCE norms were presented for FCC and HCP structural order [70, 71], and an extension subsequently proposed for five-fold symmetric ordering such as icosahedral clusters [72–74].

The premise of the algorithm is to compare the positions of the $n_b(i)$ neighbours of $i$ to a perfectly ordered reference structure $X$ with coordinations $R^X_{j=1,\ldots,n_b(i)}$. The reference coordinates must possess a set of $N_{el}$ crystallographic symmetry elements such as rotations, mirror-planes and roto-inversions. The $m$th of the $N_{el}$ crystallographic elements contains in turn $N_{g,m}$ distinct elements of the symmetry group. The CCE norm for structure $X$ is found by solving

$$
\epsilon^X(i) = \min_{S_{m,n}\in\text{SO}(3)} \sqrt{\sum_{m=1}^{N_{el}} \sum_{n=1}^{N_{g,m}} \sum_{j=1}^{n_b(i)} \left( r_j - S_{m,n} \cdot R^X_{j} \right)^2 / \sigma_{\text{ref}}^2 n_b(i) \sum_{m=1}^{N_{el}} N_{g,m}}.
$$

(3.31)

The term $S_{m,n}$ is an orthogonal matrix that performs the $n$th action of symmetry element $m$ and $\sigma_{\text{ref}}$ is a reference length that renders the norm dimensionless.

From the probability distributions of $\epsilon^X$ and given a threshold value for the structure under consideration $\epsilon_{\text{thres}}$, it is possible to calculate a global order parameter for the amount of structure $X$ within the system:

$$
s^X = \int_0^{\epsilon_{\text{thres}}} P(\epsilon^X) \, d\epsilon^X.
$$

(3.32)

The behaviour of $s^X$ for FCC and HCP crystal structures for a crystallising mixture of polymer chains is shown in figure 3.19.

The CCE is a sensitive probe of structural ordering with known symmetry in a bulk system. To our knowledge, studies have only been conducted into FCC, HCP and five-fold symmetric local ordering of bonds so far [74]. The extensibility of the algorithm may make it suited to study more exotic structural ordering, such as that found to increase on supercooling of liquids towards the glass transition [11]. Further studies along these
Figure 3.19: CCE norm analysis of a crystallising mixture of polymer chains. The analysis shows a marginal tendency for the polymer sites to crystallise into locally HCP-like order. Figure reproduced from reference [71].

lines, and studies to compare the performance of the CCE norm with the established structure detection methods, would be interesting.

3.6.8. Largest standard cluster analysis

The final structural analysis method that we consider is the largest standard cluster analysis (LSCA) method proposed by Tian et al. [75]. This method adopts a different philosophy for the neighbour network from those methods previously reviewed in this chapter. In the LSCA method the neighbours for each particle are generated dynamically during the course of the algorithm and, as such, the method does not require prior knowledge of a neighbour network. This has the advantage that no choices needs to be made as to how to generate the neighbour network.

The method incorporates ideas from the CNA and CBTIM. The structure around a single particle is decomposed in terms of modified CNA clusters termed the centre-neighbour-subclusters. Each is given an index $ijlk$ where indices $i$, $j$ and $k$ are as described in section 3.6.3 and $l$ is the longest chain of bonds between the common neighbours of the root pair. The method to construct the bonds ensures that no common neighbour of the root pair in a centre-neighbour-subcluster has more than two bonds to the other common neighbours.

A LSCA index for a particle is then given by the numbers of centre-neighbour-subclusters of each type. For instance, the LSCA index for a BCC environment is (1444-6,1666-8),
Figure 3.20: (a) The largest standard cluster analysis for the environment of a BCC. The structure of the particle and its first and second nearest neighbours is decomposed in terms of centre-neighbour-subclusters. The central particle and its neighbours each form a root pair for a centre-neighbour-subcluster. In total there are (b) eight 1666 and (c) six 1444 centre-neighbour-subclusters. The LSCA index for a BCC environment is therefore (1444-6,1666-8). Figure reproduced from [75].

The LSCA method has been used to study structural evolution in a simulation of rapidly cooled liquid silver [75]. The method is able to measure the BCC structural precursor to crystallisation into an FCC phase [76] more clearly than using BOO and CBTIM methods with a cut-off length to determine the bonds.

3.7. The Topological Cluster Classification (TCC)

The topological cluster classification (TCC) algorithm is a cluster-based method for identifying local structuring of particles. The algorithm identifies clusters within a bulk system that are defined by the ground state clusters of m isolated particles interacting with a pair-wise potential.

The algorithm works by searching a neighbour network for all three-, four- and five-membered shortest path rings of particles. The rings are categorised by the number of common neighbours to all particles in the ring, forming a set of ‘basic clusters’. Larger clusters are then identified as concatenations of the basic clusters and additional particles.

This brief summary of the TCC algorithm allows two important features of the method
(a) sp3  (b) sp4  (c) sp5

![Diagram of neighbor networks for shortest-path rings of (a) three, (b) four and (c) five particles.](image)

Figure 3.21: Neighbour networks for shortest-path rings of (a) three, (b) four and (c) five particles. Particles are denoted by black spheres and the bonds connecting them by black lines.

to be highlighted. (i) Because the ground state clusters form the candidate structures that are searched for within the bulk system by the TCC algorithm, qualitative relationships can be drawn between any structures that are identified and the interactions of the particles in the system. (ii) There is no fixed size for the structural ordering that is considered by the algorithm.

This section contains a full description of the methodology of the TCC algorithm. We proceed to define some pieces of terminology used repeatedly throughout the methodology.

If two sets of particles are being considered, for example two clusters or two shortest-path rings, we say two particles are common if they are members of both sets, and distinct or uncommon otherwise. Additional particles are particles which are not members of the immediate set under consideration.

### 3.7.1. Shortest-path rings

The starting point of the TCC algorithm is a neighbour network, as defined in section 3.5. The neighbour network is decomposed into shortest-path rings of particles [77]. Shortest-path rings are closed loops of bonded particles in the neighbour network where the shortest distance in terms of bonds between any two particles in the ring can be achieved by traversing only bonds between the ring particles. Using more formal notation, a shortest-part ring is defined as a subset of particles and bonds from the neighbour network $g \subseteq G$ where it is the case that for all particles $i$ and $j$ within the $g$ the equation $d_g(i, j) = d_G(i, j)$ holds.

The TCC method considers shortest-path rings of three, four and five particles. The neighbour networks for these shortest-path rings are shown in figure 3.21. The three-, four- and five-membered shortest path rings are denoted sp3, sp4 and sp5 respectively.

Shortest-path rings consisting of six or more particles are rarely found in systems with
short-range isotropic interactions, as studied in this thesis, and therefore are not considered here. It would be possible, however, with additional work to extend the TCC algorithm for systems with larger shortest-path rings, such as network liquids and glasses, and patchy particles.

The algorithm used to detect the shortest-path rings is similar to that described by Franzblau [77] and is depicted in figure 3.22. Starting from the neighbour network $G$, a loop proceeds over all the particles, index $i$. The three-, four- and five-membered containing $i$ are generated by the backtracking method [78]. A depth-first search proceeds over the $n_b(i)$ neighbours of $i$ with index $j > i$. If $j$ has a neighbour that is also bonded to $i$ and with index $k > j$ we have found an sp3 ring. The search then proceeds through the neighbours of $j$ and subsequently back through indices $j$ then $i$.

If no sp3 ring is identified for index combination $ijk$, the depth-first search proceeds to seek out sp4 rings $ijkl$ where $j < l$, or sp5 rings $ijklm$ where $j < m$. If no sp4 of sp5 ring is found the depth-first search halts and returns to the next neighbour $j$ of $i$. The inequality conditions stated for the particle indices ensure that each ring is detected only once when using this algorithm.

The statistics of shortest-path rings have been used as measures for local structure in their own right, for example in silica glasses [77, 79] and hard sphere crystals [48].

### 3.7.2. The basic clusters

The basic clusters are found by subdividing the shortest-path rings into three further categories. The categories are denoted by $sp_{m}a$, $sp_{m}b$ or $sp_{m}c$, where $m$ is the number of particles in the ring. For $sp_{m}a$ clusters there are no additional particles in the system that are bonded to all $m$ members of the $sp_{m}$ ring. For $sp_{m}b$ there is a single additional particle that is a neighbour of all members for the $sp_{m}$ ring. For $sp_{m}c$ there are two additional neighbours for all the $m$ ring particles. The additional particles bonded to the ring particles are termed **spindle** particles.

It is assumed that the maximum number of particles that can be bonded to any $sp_{m}$ ring is two, and that if we have an $sp_{m}c$ cluster that the two additional particles are located either side of the approximate plane defined by the shortest-path ring particles. These two assumptions are non-trivial and depend on the nature of the interactions, the state point and the method used to derive the neighbour network. The assumptions generally hold true to a good approximation if the interaction potential has a strongly repulsive core at short ranges such that there is a steric minimum distance for approach $r_{st}$ between the particles that is in practice not breached. The second requirement is that the maximum length of the bonds is only a small multiple of $r_{st}$.

The validity of these conditions are functions of the interaction potential and the method to detect the neighbours. It is prudent to check that the number of common
Particle $i$
Neighbour of $i$ with index $j > i$

Particle $j$
Neighbour of $j$ with index $k > i$

Particle $k$
Neighbour of $k$ with index $l > i$ & $l \neq j$

Particle $l$
Neighbour of $l$ with index $m > j$ & $m \neq k$

Particle $m$

next $i$

next $j$

next $k$

next $l$

next $m$

next $k$

$k$ bonded to $i$ with $k > j$

next $l$

$l$ bonded to $i$ with $l > j$

next $m$

$m$ bonded to $i$

Found sp3 ring $ijk$

Found sp4 ring $ijkl$

Found sp5 ring $ijklm$

Figure 3.22: Schematic flow diagram depicting the algorithm used to detect three-, four- and five-membered shortest-path rings.
neighbours to the ring particles is not frequently more than two in order to have confidence that the results obtained from the TCC analysis have physical significance.

For the spmc clusters, no condition is specified as to the bonding between the spindles, i.e. they may be bonded or not bonded. In practice the spindles are rarely bonded for sp3c clusters, rarely not bonded for sp5c, and bonded in around half of all instances of sp4c clusters.

In total nine basic cluster are defined, as shown in figure 3.23. The basic clusters include the first five ground state clusters of the Morse potential consisting of three or more particles. We follow the naming scheme of [80] and term the ground state clusters as 3A trimer (sp3a), 4A tetrahedron (sp3b), 5A triangular bipyramid (sp3c), 6A octahedron (sp4c) and 7A pentagonal bipyramid (sp5c). These clusters are also ground states for the LJ and Chacón-Reinaldo-Falagán-Velasco-Tarazona (CRVT) potentials (see appendix A).

3.7.3. Compound clusters

In the following sections the detection routines for larger clusters that are identified starting from the basic clusters are described. These clusters are termed compound clusters. They consist of either multiple smaller clusters (either basic or other compound clusters) or a single sub-cluster and additional particles that are bonded to it.

For each compound cluster a number of conditions are given for it to be detected.
These conditions are stated in terms of how the constituent particles, either spindle, ring, or additional particles are connected by bonds. The conditions are in general satisfied by a number of subtly different bond networks \{g_{GC}\} that we term the TCC bond networks for a ground state cluster. The TCC bond networks are similar to the bond network of the ground state configuration of the cluster \(g_{gs}\). Detecting structure in terms of multiple bond networks allows for some degree of thermally induced distortion of the cluster in the bulk relative to the ground state structure.

The simple aims for a detection routine for a compound cluster is that it is (i) accurate in detecting a given type of order and (ii) simple to implement computationally. If the conditions that a routine imposes for a particular cluster to exist are overly restrictive, thermal fluctuations may mean that detection of the structure in a bulk system is rare. Likewise if the conditions are not sufficiently prescriptive, the order may be detected spuriously or conflicting types of order detected in the same locality.

For the first of the stated aims, the accuracy of detection will be a function of the system under study, the state point and the method used to detect the bonds. The following three general principles are followed relative to the ground state bond network in order to maximise the accuracy of the routines:

1. The short-path rings of particles from basic cluster must lie approximately in a plane in the ground state configuration of the cluster.
2. The bonds that are required for the structure to exist should all be of similar in length in the ground state bond network.
3. The ratio between the shortest bond that if in place would break the detection of the cluster to the longest bond required for the cluster to exist should be maximised (where the bond lengths are taken from the ground state configuration).

Simplicity of the routines is achieved by utilising the largest sub-clusters where possible from the ground state bond network for the cluster. If multiple sub-clusters are going to be required to detect the cluster, the overlap between the sub-clusters should be minimised. Obeying these suggestions generally minimises the number of conditions needed to detect the cluster.

A summary of how the detection routines for the compound TCC clusters are devised is as follows:

1. A configuration of particle positions for a cluster is found by identifying a global or local minimum of the potential energy landscape for a given potential. The minimisation is performed using the method described in [81].
2. The bond network is found for this configuration using a reference neighbour detection method. In the case of the Morse, LJ and Wahnström models, this is the modified Voronoi method with $f_c = 0.82$. The value $f_c = 1.0$ is used for the Kob-Andersen (KA) model.

3. The basic clusters and other smaller compound clusters are identified from within the bond network.

4. A set of sub-clusters that contain all the particles (perhaps with the inclusion of one or two additional particles) is chosen and the detection routine is based upon these sub-clusters.

5. The sub-clusters chosen tend to be the largest available in the bond network, whilst ensuring that the three previously stated principles are obeyed as closely as possible.

6. Conditions are imposed on the particles shared between sub-clusters and the bonds required between the sub-clusters and additional particles for the structure to exist. The bonds are selected using principles 2 and 3 stated above.

Detection of clusters is hierarchical: smaller sub-clusters must be detected prior to larger compound clusters.

The naming scheme for the TCC clusters follows from Doye et al. [80, 82] for the ground state clusters of the Morse potential. A cluster symbol (CS) $mX$ describes the number of particles in the cluster ($m$) and a character $X$ denotes the potential for which the cluster is a ground state configuration. The characters X=A,B,C... indicate the range $\rho_0$ of the Morse potential for which the cluster is a ground state, where A is for the longest ranges, and B, C, ... indicate increasingly short range attractions (i.e. increasing $\rho_0$). The shortest range Morse potential considered in [82] is $\rho_0 = 25$.

The 6Z cluster is the ground state cluster for six particles of the Dzugutov potential [83] and only a local minimum of the Morse interaction potential for 6 particles. Its detection routine is included as it is a free energy minimum cluster for six colloids with depletion-mediated attractions (see chapter 4). Ground state clusters specific to binary KA and Wahnström LJ potentials are denoted by characters ‘K’ and ‘W’ respectively.

The ground state clusters and their energies for each potential employed in simulations in this thesis are listed in appendix A. For each ground state cluster the appropriate TCC CS is given.

3.7.4. $m = 6$ to 9 compound clusters

In the following sections the symbol $s$ is used to denote the index of a spindle particle in a basic cluster, $r$ to denote a ring particle, and $a$ an additional particle. The subscripts $c$
Figure 3.24: The (a) 6Z and (b) 7A clusters. The two sp3 rings of the 5A clusters are shown in white (5A\textsubscript{i}) and blue (5A\textsubscript{j}).

and d on a particle index denote common and distinct particles respectively. Sub-clusters are referenced by the indices \textit{i}, \textit{j}, \textit{k}, ....

\textbf{6Z}

The 6Z cluster is the ground state for six particles interacting with the Dzugutov potential \cite{83}. It is also a local minimum of the Morse potential. It consists of a pair of 5A clusters where:

1. The are no common spindles between the two 5A clusters.
2. One spindle of 5A\textsubscript{i} is common with a sp3 ring particle of 5A\textsubscript{j}.
3. One spindle of 5A\textsubscript{j} is common with a sp3 ring particle of 5A\textsubscript{i}.
4. The spindles in the two sp3 rings are bonded.
5. Two particles are common between the sp3 rings of 5A\textsubscript{i} and 5A\textsubscript{j}.

\textbf{7K}

The 7K cluster is the ground state of KA LJ for seven particles. In the ground state there are four of the larger \textit{A}-species particles. We give a detection routine based on the bond network of the ground state cluster as detected when using the modified Voronoi method with \(f_c = 1.0\). The cluster is similar to a 7A cluster, but one of the sp5 ring particles is drawn towards the centre of the ring. It is detected using a pair of 5A clusters where:

1. 5A\textsubscript{i} and 5A\textsubscript{j} have one common spindle particle.
2. The other spindle of 5A\textsubscript{i} is distinct from all the particles in 5A\textsubscript{j}.
3. The other spindle of 5A<sub>j</sub> is distinct from all the particles in 5A<sub>i</sub>.

4. There are two common particles between the sp3 rings of 5A<sub>i</sub> and 5A<sub>j</sub>.

The ratio of the longest to the shortest bond in neighbour network of the ground state cluster is 1.26. Both these bond types must be in place in the bulk system for the cluster to be detected by the TCC algorithm.

**8A**

The 8A cluster is the ground state of the Morse potential for range $\rho_0 < 5.28$. It consists of two sp5b/c clusters and three detection routines are necessary.

(i) A pair of sp5b clusters:

1. The spindle particles are distinct.
2. There are four common particles between sp5 rings of sp5b<sub>i</sub> and sp5b<sub>j</sub>.

(ii) A pair of 7A clusters:

1. Both 7A<sub>i</sub> spindle particles are common with the 7A<sub>j</sub> spindles.
2. There are four common particles between sp5 rings of 7A<sub>i</sub> and 7A<sub>j</sub>.

(iii) A sp5b cluster and a 7A cluster:

1. One 7A spindle is common with the sp5b spindle.
Figure 3.26: The (a) 8K and (b) 9A clusters. Pink bonds indicate the shortest-path ring in the \( k \)th sub-cluster involved in the detection of 8K and 9A.

2. The other 7A spindle is distinct from all the sp5b particles.

3. There are four common particles between sp5 rings of sp5b and 7A.

8B

The 8B cluster is the ground state of the Morse potential for range \( 5.28 \leq \rho_0 < 25 \). It consists of a 7A cluster and with one additional particle

1. The additional particle is bonded to one 7A spindle.

2. The additional particle is bonded to two neighbouring particles in the sp5 ring particles of 7A.

8K

The 8K cluster is the ground state of KA LJ for eight particles, and contains five of the larger A-species particles. It consists of three 5A clusters:

1. Two common particles in the sp3 rings of 5A\(_i\), 5A\(_j\) and 5A\(_k\).

2. One common spindle between 5A\(_i\) and 5A\(_j\).

3. One common spindle between 5A\(_i\) and 5A\(_k\).

4. One common spindle between 5A\(_j\) and 5A\(_k\).

5. One particle in sp3 ring of 5A\(_i\) is not in 5A\(_j\) and 5A\(_k\).
Figure 3.27: The (a) 9B and (b) 9K clusters.

6. One particle in sp3 ring of 5A_j is not in 5A_i and 5A_k.

7. One particle in sp3 ring of 5A_k is not in 5A_i and 5A_j.

9A

The 9A cluster is the ground state for the Morse potential for range \( \rho_0 < 3.42 \). Three sp4b clusters combine as:

1. The three spindle particles are distinct.

2. There are no bonds between the three spindle particles.

3. There are two common particles between sp4 rings of sp4b_i and sp4b_j.

4. The distinct particles between the sp4 rings of sp4b_i and sp4b_j form the sp4 ring of sp4b_k.

9B

The 9B cluster is the ground state for the Morse potential for range \( 3.42 \leq \rho_0 < 25 \). It consists of two 7A clusters where:

1. There is one common spindle particle.

2. The distinct spindle particles are bonded.

3. The distinct spindle of 7A_i is common with an sp5 ring particle of 7A_j.
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3.75. $m = 10$ compound clusters

**10A**

The 10A cluster is the ground state for the Morse potential for range $\rho_0 < 2.28$. Two sp4b clusters are used for its detection:

4. The distinct spindle of 7A$_j$ is common with an sp5 ring particle of 7A$_i$.

5. There are two common particles between the sp5 rings of 7A$_i$ and 7A$_j$.

**9K**

The 9K cluster is the ground state of KA LJ for nine particles, where six of the particles are the larger A-species. There are two 6A clusters that combine as:

1. One common spindle particle.

2. The uncommon spindle of 6A$_i$ is distinct from 6A$_j$.

3. The uncommon spindle of 6A$_j$ is distinct from 6A$_i$.

4. There are two common particles between sp4 rings of 6A$_i$ and 6A$_j$.

5. The common sp4 ring particles are bonded.
1. All the particles in $sp4b_i$ and $sp4b_j$ are distinct.
2. The spindle particles of $sp4b_i$ and $sp4b_j$ are not bonded.
3. Each particle of $sp4$ ring of $sp4b_i$ is bonded to exactly two particles in $sp4b_j$.
4. Each particle of $sp4$ ring of $sp4b_j$ is bonded to exactly two particles in $sp4b_i$.

**10B**

The 10B cluster is the ground state for the Morse potential for range $2.28 \leq \rho_0 < 25$. The detection routine presented decomposes 10B as a 9B and a 7A cluster. The 10B cluster is the first compound cluster where its detection routine relies on a sub-cluster that is also a compound cluster (9B). It is equally valid to formulate the detection of 10B in terms of three 7A clusters if prior detection of 9B clusters is not of interest.

1. One spindle from 7A is common to the ‘common spindle particle’ of the 9B cluster (see section 3.7.4).
2. The other spindle from 7A is bonded to the two distinct spindles of 9B.
3. Two sp5 ring particles from 7A are common with the distinct spindles of 9B.
4. Two sp5 ring particles from 7A are common with the distinct sp5 particles of 9B.
5. The final sp5 ring particle from 7A is distinct from the 9B cluster.

**10K**

The 10K cluster is the ground state of KA LJ mixture for ten particles, where seven of the particles are the $A$-species. It consists of a 9K cluster with one additional particle:

1. The common spindle particle in 9K has one additional neighbour that is distinct from all of the other 9K particles.

**10W**

The 10W cluster is only a local minimum of the Wahnström LJ potential for ten particles with nine $A$-species. It is included for completeness such that all the energy minimum
clusters for each composition of $m_A$ $A$-species for $m$ Wahnström particles are included in the TCC algorithm (see appendix A). The cluster consists of six sp5b clusters where:

1. All of the spindles are common.

2. The common spindle has coordination number 9.
3.7.6. \( m = 11 \) compound clusters

11A

The 11A cluster is the ground state for eleven Morse particles for range \( \rho_0 < 3.40 \). Two 6A clusters are combined as:

1. One common spindle particle.
2. All other particles in 6A\(_i\) are distinct from those in 6A\(_j\).
3. Each particle in the sp4 ring 6A\(_i\) is bonded to two particles in sp4 ring of 6A\(_j\).
4. Each particle in the sp4 ring 6A\(_j\) is bonded to two particles in sp4 ring of 6A\(_i\).

The ground state cluster for the Morse potential \( \rho_0 = 3 \) is considered to understand the nature of the bonds required to be in place in order that 11A is detected by this routine. The ratio of the lengths of the longest bond to the shortest bond required is 1.27. The longest bonds are those bonds between the sp4 rings of the 6A clusters. The shortest bonds are between the common spindle and the sp4 ring particles. Relatively few 11A clusters are detected when using a bond network that discounts long bonds, e.g. when using a short cut-off length or a low value of \( f_c \), as thermal fluctuations cause the bonds between the sp4 ring particles to break and the cluster to go undetected.

For the KA liquid studied in chapter 7 the 11A cluster has previously been identified as relevant for the glassy behaviour \([11]\). The KA ground state cluster is topologically equivalent to 11A, i.e. it has the same bond network, but the relative lengths are different due to its composition in terms of eight A- and three B-species. The ratio of the longest to the shortest bonds is 1.23 and this is large enough to cause poor detection of the 11A cluster when using the modified Voronoi method with \( f_c = 0.82 \). Therefore the value \( f_c = 1.0 \) is used to determine the neighbours when studying the KA system in later chapters.

11B

The 11B cluster is the ground state for eleven Morse particles for range \( 3.40 \geq \rho_0 < 3.67 \). It is a compound of a 9B cluster and two additional particles. The particles in the 9B cluster that are not the common spindle are termed the shell particles.
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Figure 3.31: The (a) 11C and (b) 11E clusters. (a) Particle \( r_{d1} \) is a neighbour of \( r_{d2} \), and \( r_{d3} \) is a neighbour of \( r_{d4} \). Particles \( r_{d5} \) and \( r_{d6} \) are not neighbours.

1. The common spindle particle from the 9B cluster has coordination number 10.

2. The two additional particles are bonded to each other and to the common spindle particle of 9B.

3. Each additional particle is bonded to two more particles in the shell of the 9B cluster, leading to a total of four bonds between the additional particles and 9B.

4. For each additional particle, the two shell particles to which they are bonded are not themselves bonded.

5. The four shell particles of the 9B cluster that are bonded to the two additional particles form two pairs that are neighbours.

11C/D

There are two ground state clusters of eleven particles for the Morse potential for range \( 3.67 \leq \rho_0 < 13.57 \), namely 11C and 11D. Both these clusters have identical ground state bond networks, so are not distinguished between by the TCC algorithm. We term both clusters 11C and detected them as a combination of two 7A clusters:

1. There is one common spindle particle.

2. There are two further common particles between 7A\(_i\) and 7A\(_j\). These are a bonded pair in the sp5 rings of 7A\(_i\) and 7A\(_j\).

3. There are two further bonds between distinct particles in the sp5 rings of 7A\(_i\) and 7A\(_j\).
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Figure 3.32: The (a) 11F and (b) 11W clusters. (a) The white and blue sp3 rings are indicate the 5A clusters, and the pink and green sp4 rings indicate the 6A clusters. Only the spindles of the 5A clusters are highlighted in yellow. (b) The additional neighbour \( a \) of the common spindle \( s_c \) in the 10B cluster is highlighted.

11E

The 11E cluster is the ground state for eleven Morse particles with the range of the potential \( 13.57 \leq \rho_0 < 20.60 \). Two clusters are used for its detection routine, 9B and 7A:

1. One 7A spindle particle is common to one of the uncommon spindle particles, \( s_{d1} \), in the 7A clusters constituting the 9B cluster.

2. The other spindle particle of the additional 7A is labeled \( s_{d3} \) and is bonded to the other uncommon spindle particle \( s_{d2} \) in 9B and the common spindle particle \( s_c \) of 9B.

3. Of the 7A cluster sp5 ring particles, one is common to the common with \( s_c \), one is common with \( s_{d2} \), and one is common to one of the uncommon sp5 ring particles of the 9B cluster (\( r \) in figure 3.31). The final two sp5 ring particles are distinct from the 9B cluster.

11F

The 11F cluster is the ground state for eleven Morse particles with the range of the potential \( 20.60 \leq \rho_0 < 25 \). It consists of two 5A and two 6A clusters:

1. Each spindle in 5A\(_i\) is bonded to one spindle in 5A\(_j\) and vice versa. Thus there are
two pairs of bonded spindles, \((s_{t1}, s_{t2})\) and \((s_{b1}, s_{b2})\).

2. There is one common particle between the sp3 ring of \(5A_i\) and \(5A_j\), \(r_c\).

3. There is one bond between the other particles in sp3 rings of \(5A_i\) and \(5A_j\), forming a pair \((r_{d1}, r_{d2})\).

4. \(6A_k\) has one spindle in common with \(r_c\), and the other spindle is distinct from \(5A_i\), \(5A_j\) and \(6A_l\). Its sp4 ring particles are \(r_{d1}, r_{d2}, s_{t1}, s_{t1}\).

5. \(6A_l\) has one spindle in common with \(r_c\), and the other spindle is distinct from \(5A_i\), \(5A_j\) and \(6A_k\). Its sp4 ring particles are \(r_{d1}, r_{d2}, s_{b1}, s_{b1}\).

11W

The 11W cluster is the ground state of Wahnström LJ mixture for eleven particles. Nine of the particles are the larger \(A\)-species. A 10B cluster and an additional particle come together where:

1. The common spindle of the 10B cluster has coordination number 10.

2. The additional particle is not bonded to any of the distinct spindles of the 7A clusters constituting the 10B cluster.

3.7.7. \(m = 12\) compound clusters

12A

The 12A cluster is the ground state for twelve Morse particles with the range of the potential \(\rho_0 < 2.63\). It consists of an 11C cluster with one additional particle:

1. The common spindle particle of the 11C has coordination number 11.

2. The additional particle is bonded to three particles in the 11C cluster: the common spindle, and the two sp5 ring particles of the 7A clusters constituting 11C that are not bonded to any of the other 7A cluster’s particles \((r_{d5} \text{ and } r_{d6} \text{ in figure 3.31(a)})\).
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Figure 3.33: The (a) 12A and (b) 12B clusters. (a) The additional particle is bonded only to \( s_c, r_{d5} \) and \( r_{d6} \). (b) Five 7A clusters have spindles \( s_c \) and \( s_1 \) to \( s_5 \), the latter being bonded to \( s_d \) of the central 7A cluster.

12B/C

There are two ground state clusters of twelve particles for the Morse potential for range \( 2.63 \leq \rho_0 < 12.15 \), namely 12B and 12C. Both these clusters have identical ground state bond networks and so cannot be distinguished between by the TCC algorithm. We term both clusters 12B and detected them as six 7A clusters where:

1. There is one central 7A cluster with spindles \( s_c \) and \( s_d \).
2. The other five 7A clusters have one spindle given by \( s_c \) and one spindle bonded to \( s_d \).

12D

The 12D cluster is the ground state for twelve Morse particles with the range of the potential \( 12.15 \leq \rho_0 < 17.08 \). A 7A cluster is appended to an 11E cluster where:

1. The spindle particles of the 7A cluster are common with 11E cluster spindles \( s_{d2} \) and \( s_{d3} \).
2. Of the sp5 ring particles of the 7A cluster, one is common to \( s_c \), one is common to \( s_{d1} \), two are in the sp5 rings of the 7A clusters constituting 11E (\( r_{c1} \) and \( r_{c2} \) in figure 3.34(a)), and one is new.
Figure 3.34: The (a) 12D and (b) 12E clusters. (a) The 7A cluster added to the 11E cluster has its sp5 ring highlighted with green bonds. (b) The additional 5A cluster to the 11F cluster has its sp3 ring highlighted with white bonds and its spindles are $s_{t3}$ and $s_{b3}$.

12E

The 12E cluster is the final Morse cluster for twelve particles. It is the ground state for range $17.08 \leq \rho_0 < 25$. One 11F cluster and one 5A cluster combine as:

1. The spindle atoms of the 5A cluster are common with the uncommon spindle atoms of the 6A clusters constituting the 11F cluster.

2. Of the sp3 ring particles in the 5A cluster, two are common with $r_{d1}$ and $r_{d2}$ from the 11F cluster, and one is new.

12K

The 12K cluster is the ground state of \textit{KA LJ} mixture for twelve particles, where eight of the particles are the larger $A$-species. It consists of an 11A cluster with one additional particle:

1. The additional particle is bonded to three mutually bonded sp4 ring particles in the 6A clusters that constitute the 11A cluster.
Figure 3.35: The (a) 12K and (b) 13A clusters. (a) The additional particle \( a \) is bonded to particles \( r_{d1} \), \( r_{d2} \) and \( r_{d3} \) in the sp4 rings of the 11A cluster.

3.7.8. \( m = 13 \) compound clusters

13A

The 13A cluster is the ground state for thirteen Morse particles with the range of the potential \( \rho_0 < 14.76 \). This cluster is topologically equivalent to the icosahedral cluster discussed by Frank [35]. One 12B cluster is supplemented with a 7A cluster:

1. The 7A cluster has one spindle given by \( s_c \) of the 12B cluster, and one spindle that is distinct from the 12B particles.

2. The sp5 ring particles of the 7A cluster are distinct from the sp5 ring particles of the central 7A cluster in 12B.

13B

The 13B cluster is the ground state for thirteen Morse particles with the range of the potential \( 14.76 \leq \rho_0 < 25 \). There are two 7A clusters:

1. There is one common particle between \( 7A_i \) and \( 7A_j \), which is a spindle \( s_c \).

2. Other spindle particles are distinct and not bonded.

3. Each particle from sp5 ring of \( 7A_i \) is bonded to one sp5 particle of \( 7A_j \).

4. Each particle from sp5 ring of \( 7A_j \) is bonded to one sp5 particle of \( 7A_i \).
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Figure 3.36: The (a) 13B and (b) 13K clusters. (a) Each sp5 ring particle from one 7A clusters is bonded to a single sp5 ring particle in the other 7A cluster. (b) The sp3 rings of the additional 5A clusters are not shown.

13K

The 13K cluster is the ground state of KA LJ mixture for thirteen particles, where seven of the particles are the larger A-sppcies. An 11F cluster sees two additional 5A clusters:

1. Cluster 5A\textsubscript{i} has spindles \( s_{t1}, s_{b1} \).

2. The sp3 ring particles of 5A\textsubscript{i} are \( r_c \) and the other sp3 ring particle from the 5A cluster in 11F with spindles \( s_{t1}, s_{b1} \) that is not \( r_{d1} \) in figure 3.32(a). The third sp3 ring particle from 5A\textsubscript{i} is distinct from the 11F cluster.

3. Cluster 5A\textsubscript{j} has spindles \( s_{t2}, s_{b2} \).

4. The sp3 ring particles of 5A\textsubscript{j} are \( r_c \) and the other sp3 ring particle from the 5A cluster in 11F with spindles \( s_{t2}, s_{b2} \) that is not \( r_{d2} \) in figure 3.32(a). The third sp3 ring particle from 5A\textsubscript{j} is distinct from the 11F cluster.

3.7.9. Crystal clusters

In order to detect crystalline structure and to test the performance of the TCC algorithm against phases with known structure, detection routines are implemented for crystalline clusters.
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Figure 3.37: The (a) FCC and (b) HCP clusters. (a) The six-membered ring consists of the gray particles in the horizontal plane around $s_c$. (b) The six-membered ring consists of the gray particles in the horizontal plane around $r_c$.

**FCC**

The $m = 13$ FCC cluster is a particle and its first-nearest neighbours as taken from a FCC crystal lattice. It is a compound of either four sp3b clusters or three sp3b clusters and a 5A cluster:

1. The spindle particles of sp3b$_i$, sp3b$_j$, and sp3b$_k$ are all bonded to each other.

2. There is one common particle $s_c$ between sp3b$_i$, sp3b$_j$, and sp3b$_k$, which is in the sp3 ring of each cluster. The rest of the particles are distinct.

3. One of the uncommon sp3 ring particles in sp3b$_i$ is bonded to one uncommon sp3 ring particle in sp3b$_j$, and the other is bonded to one uncommon ring particle in sp3b$_k$.

4. One of the uncommon sp3 ring particles in sp3b$_j$ is bonded to one uncommon sp3 ring particle in sp3b$_i$, and the other is bonded to one uncommon ring particle in sp3b$_k$.

5. One of the uncommon sp3 ring particles in sp3b$_k$ is bonded to one uncommon sp3 ring particle in sp3b$_i$, and the other is bonded to one uncommon ring particle in sp3b$_j$.

Excluding the spindle particles, we now have a six-membered ring of particles around $s_c$. The six-membered ring defines six sp3 rings with $s_c$, three of which were the sp3 rings for sp3b$_i$, sp3b$_j$, and sp3b$_k$, and three of which are new.
1. The fourth sp3b cluster or the 5A cluster have a spindle \( s_c \). Each sp3 particle in the fourth cluster forms an sp3b cluster with each of the new sp3 rings from the six-membered ring around \( s_c \).

If the fourth cluster is a 5A cluster, its spindle that is not \( s_c \) is not counted as part of the FCC cluster.

**HCP**

The \( m = 13 \) HCP cluster is a particle and its neighbours taken from a HCP crystal lattice. It is a compound of three 5A clusters:

1. There is one common particle \( r_c \) between 5A\(_i\), 5A\(_j\) and 5A\(_k\) that is in the sp3 ring of each cluster.

2. The spindle atoms from 5A\(_i\), 5A\(_j\) and 5A\(_k\) form two sp3 rings (\( s_{t1}, s_{t2}, s_{t3} \)) and (\( s_{b1}, s_{b2}, s_{b3} \)).

3. Within the three 5A clusters, the spindle atoms are only bonded to the particles from the cluster’s own sp3 ring.

4. The uncommon sp3 ring particles from 5A\(_i\), 5A\(_j\) and 5A\(_k\) form a six-membered ring around \( r_c \), i.e. each is bonded to a single particle from any of the other cluster’s uncommon sp3 ring particles.

**9X**

The 9X cluster is found in the ground state FCC and BCC crystal lattices. However the size of the cluster means that it does not uniquely determine crystalline order (in the same manner that tetrahedral order, although found in all bulk crystalline states, does not imply crystallinity). It is a compound of either two sp4b clusters, two 6A clusters, or a sp4b cluster and a 6A cluster:

1. There is one common particle between the clusters, which is a spindle particle.

2. Each of the particles in the two sp4 rings of the constituent clusters is bonded to one particle in the other sp4 ring.
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3.7.10. Notes on computation

Here we pay attention as to how to implement the cluster detection routines efficiently. Starting from the shortest-path rings, the basic clusters are identified by looping through all the neighbours of one particle in the short-path ring and checking how many are bonded to the other particles in the shortest-path ring. This identifies all of the basic clusters.

The sp3b and 6A clusters are highly symmetrical with sp3b consisting of four sp3 rings and 6A of up to three sp4 rings. It is necessary to enumerate each of these instances separately because the detection of compound clusters using sp3b and 6A depends on the orientation of the shortest-path rings in these basic clusters.

For all the other clusters, however, it is only necessary to detect each instance once. This can be achieved by looping through each of the sub-clusters in increasing index of the order in which they were detected. For example, 6Z would be detected by first looping over all 5A clusters index $i$, and searching for an appropriate 5A cluster to pair with by looping over 5A clusters with index $j > i$.

For large systems simple nested loops over the sub-clusters in a compound cluster will become prohibitively expensive to compute as the number of clusters increases approximately $O(N)$ in the system size. In this case the speed of computation can be
improved by maintaining a list of all the indices of the sub-clusters that each particle is a member of. The nested loops over all sub-clusters can then be replaced by loops over all of the sub-clusters that a chosen particle is a member of. The chosen particle must necessarily be a member of all candidate sub-clusters, and can either be part of or a neighbour of the sub-cluster in the next highest loop in the sequence. The effect of this modification is to check only candidate sub-clusters that can possibly meet the conditions imposed for the larger cluster to exist.

As a practical example, this algorithm is implemented for the 6Z cluster by replacing the loop over $5A_j$ clusters where $j > i$ with a loop over all $5A_j$ clusters that the first particle in the sp3 ring of $5A_i$ is a member of. A check is implemented to ensure that $j > i$ (in order to find each 6Z only once) and detection of 6Z proceeds as before.

For the 10A cluster, sp4b$_j$ candidates must be chosen from neighbours of the first particle in the sp4 ring of sp4b$_i$. This is because there is no overlap between the sp4b$_i$ and sp4b$_j$ clusters in 10A.

### 3.7.11. Summary of clusters

A summary of all the TCC clusters is given in table 3.2. Each cluster is identified by a cluster symbol (CS). The reference potential used to generate a configuration for a ground state cluster is listed.

As the detection method for each cluster is devised using a reference bond network it is not certain that the TCC algorithm will correctly detect the same cluster if a different bond network is supplied to the algorithm. In practice there are only a few cases when a cluster is not detected when using a bond network different from the reference network, at least when using the simple cut-off or modified Voronoi $f_c = 0.82$, 1 methods that we have considered.

Specifically the Morse clusters 8A, 9A, 10A and 11B fail to satisfy one or more of the conditions for the clusters to exist when additional long bonds are identified using the modified Voronoi method with $f_c = 1$ on the ground state configuration. Conversely the KA clusters 7K and 8K are not found using $f_c = 0.82$ as the detection routine relies on the existence of bonds identified when $f_c = 1$.

We consider the stability of the TCC cluster detection to fluctuations in bond lengths by examining the lengths of the bonds in the ground state bond networks for each clus-
<table>
<thead>
<tr>
<th>CS</th>
<th>Potential</th>
<th>$f_c = 0.82$</th>
<th>$f_c = 1$</th>
<th>$r_i/r_s$</th>
<th>$r_b/r_s$</th>
<th>$r_b/\eta$</th>
<th>CNA / VFA</th>
</tr>
</thead>
<tbody>
<tr>
<td>3A</td>
<td>$\rho_0 = 6$</td>
<td>●</td>
<td>●</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4A</td>
<td>$\rho_0 = 6$</td>
<td>●</td>
<td>●</td>
<td>1</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
| 5A  | $\rho_0 = 6$ | ● | ● | 1 | | | | CNA-2331
| 6A  | $\rho_0 = 6$ | ● | ● | 1 | 1.41 | 1.41 | CNA-1441 / 2441
| 6Z  | $\rho_0 = 6$ | ● | ● | 1 | 1.63 | 1.63 | |
| 7A  | $\rho_0 = 6$ | ● | ● | 1.01 | 1.62 | 1.61 | CNA-1551
| 7K  | KA $m_A = 4$ | (7A) | ● | 1.26 | 1.78 | 1.41 | CNA-1551
| 8A  | $\rho_0 = 6$ | ● | 1.02 | 1.28 | 1.26 | |
| 8B  | $\rho_0 = 6$ | ● | ● | 1.01 | 1.64 | 1.62 | |
| 8K  | KA $m_A = 5$ | ● | 1.29 | 1.91 | 1.48 | | CNA-1661
| 9A  | $\rho_0 = 6$ | ● | 1.01 | 1.41 | 1.4 | |
| 9B  | $\rho_0 = 6$ | ● | ● | 1.01 | 1.62 | 1.59 | |
| 9K  | KA $m_A = 6$ | ● | ● | 1.26 | 1.75 | 1.39 | |
| 10A | $\rho_0 = 6$ | ● | 1.01 | 1.41 | 1.4 | |
| 10B | $\rho_0 = 6$ | ● | ● | 1.03 | 1.65 | 1.59 | |
| 10K | KA $m_A = 7$ | ● | ● | 1.29 | 1.76 | 1.37 | |
| 10W | Wahn $m_A = 9$ | ● | ● | 1.16 | 1.49 | 1.28 | VFA-(0,0,9)
| 11A | $\rho_0 = 3$ | ● | 1.27 | 1.79 | 1.41 | | VFA-(0,2,8)
| 11B | $\rho_0 = 3.6$ | ● | 1.18 | 1.3 | 1.11 | | VFA-(0,2,6,2)
| 11C | $\rho_0 = 6$ | ● | ● | 1.06 | 1.67 | 1.58 | |
| 11E | $\rho_0 = 6$ | ● | ● | 1.03 | 1.65 | 1.6 | |
| 11F | $\rho_0 = 6$ | ● | ● | 1.01 | 1.42 | 1.41 | |
| 11W | Wahn $m_A = 8$ | ● | ● | 1.24 | 1.78 | 1.44 | VFA-(0,1,6,3)
| 12A | $\rho_0 = 2.5$ | ● | 1.2 | 1.36 | 1.13 | | VFA-(1,0,6,4)
| 12B | $\rho_0 = 6$ | ● | ● | 1.07 | 1.69 | 1.58 | |
| 12D | $\rho_0 = 6$ | ● | ● | 1.04 | 1.66 | 1.6 | |
| 12E | $\rho_0 = 6$ | ● | ● | 1.01 | 1.42 | 1.41 | |
| 12K | KA $m_A = 8$ | ● | ● | 1.26 | 1.4 | 1.12 | |
| 13A | $\rho_0 = 6$ | ● | ● | 1.05 | 1.7 | 1.62 | VFA-(0,0,12)
| 13B | $\rho_0 = 14$ | ● | ● | 1.02 | 1.43 | 1.41 | VFA-(0,10,2)
| 13K | KA $m_A = 7$ | ● | ● | 1.29 | 1.76 | 1.36 | |
| FCC | Bulk FCC | ● | 1 | 1.41 | 1.41 | | VFA-(0,12)
| HCP | Bulk HCP | ● | 1 | 1.41 | 1.41 | | VFA-(0,12)
| 9X  | Bulk BCC | ● | ● | 1.15 | 1.63 | 1.41 | |

Table 3.2: Summary of the clusters detected by the TCC algorithm. **CS** is the name of each cluster. The second column contains details for the reference potential used to make a configuration of the ground state cluster. The bullets in the $f_c$ columns indicate if the TCC algorithm successfully detects the cluster in its ground state configuration. The lengths $r_s$, and $\eta$ are the shortest and longest bonds required in the ground state bond network in order that the TCC algorithm successfully detects the cluster. The length $r_b$ is for the shortest bond that could form and result in the cluster no longer being detected. The final column contains suggestions for CNA and VFA clusters with structure similar to the TCC clusters.
Specifically we consider the lengths of the shortest \( r_s \) and longest bonds \( r_l \) that are required to exist for the reference ground state configuration of a cluster to be correctly detected as that structure. If the ratio \( r_l/r_s \) is large a bond detection method that includes bonds longer than \( r_l \) is necessary in order to successfully detect the cluster.

As a rule of thumb, the Morse ground state clusters have \( r_l/r_s \approx 1 \) meaning that the bonds utilised by the TCC detection routines for these clusters are all of similar length. Exceptions to this rule are the 11A, 11B and 12B clusters, where better detection performance is obtained by using a neighbour detection method that includes bonds with a wider range of lengths, for example the modified Voronoi with \( f_c \rightarrow 1 \). The KA and Wahnström clusters also have relatively large ratios for \( r_l/r_s \) and a careful choice for the bond detection method is necessary to determine structural order accurately relative to the ground state clusters for these systems.

We also consider the shortest length \( r_b \) of any additional bond that if included in the bond network would not satisfy one of the conditions for the cluster to exist. The ratio \( r_b/r_s \) indicates the relative lengthscale of this additional bond.

The ratio \( r_b/r_l \) contains information on the robustness of the detection routine for each cluster. A large value of \( r_b/r_l \) indicates that there is a large separation between the longest bond required for the cluster to be detected, and the shortest bond that if included results in the cluster going undetected. Clusters with low values of \( r_b/r_l \), for example 8A, 10W, 11B, 12A, and 12K, are difficult to identify reliably in thermal systems.

Some of the ground state clusters with detection routines implemented by the TCC have similar structures to the clusters identified by the CNA and VFA method. Specifically these are the clusters based around a pair of particles or are a central particle and its complete first coordination shell of neighbours. For these clusters the most similar CNA and VFA clusters are suggested in the final column of table 3.2.

### 3.7.12. Example systems: LJ crystals and liquid

We demonstrate the TCC algorithm on the simulations of four LJ phases first discussed in section 3.5.6.

Figure 3.39 shows the ensemble average of the number of FCC and HCP crystal clusters \( N_C \) versus modified Voronoi parameter \( f_c \) for the FCC and HCP phases. For comparison the number of (0,12) clusters is shown for the two phases as obtained with the VFA
Figure 3.39: Comparison of the detection of FCC and HCP crystalline order with the TCC and VFA methods. The number of FCC, HCP and VFA-(0,12) clusters is \( N_C \). MC LJ simulations at \( T = 0.92, P = 5.68 \).

For all values of \( f_c \) the TCC algorithm finds more of the crystal clusters than the VFA method because the TCC detection routines allow for a greater distortion of the order by thermal fluctuations. For both methods the number of clusters tends to zero as \( f_c \rightarrow 1 \), because of the tendency of the bond detection method to over-estimate the true number of nearest neighbours by including long bonds. The number of clusters identified also tends to zero for low values of \( f_c \) as the bond detection method does not all of the nearest neighbors.

The optimal value of \( f_c \) for best detection of the crystalline order across both phases and methods is close to the value of \( f_c = 0.82 \) originally proposed by Williams [34].

In figure 3.40(a) the fraction of particles detection within each cluster type is shown for each phase, where \( N_C \) is the number of particles detected within each cluster type.

The discussion begins by analysing the detection of crystalline FCC and HCP clusters in their respective bulk phases, as this offers a test of the method for phases with known local structure. All particles are found within FCC and HCP clusters, i.e. \( N_C/N \approx 1 \) for the respective crystalline phases. We note that \( N_C \leq N_C^{\text{FCC}} \) and HCP clusters (cf. figure 3.39) as the former measure is equivalent to counting the number of particles at the centre of the crystal clusters while the latter also includes particles in the shells of crystal clusters even if they are not themselves at the centre of a crystal cluster.

For the FCC crystal phase, 6A and 9X clusters are detected in large quantities. This result is expected as these clusters form part of the ground state structure of the FCC
Figure 3.40: Detection of the LJ ground state clusters with the TCC algorithm. The bond detection method is modified Voronoi method with $f_c = 0.82$. (a) Fraction of particles detected within each cluster type. (b) Potential energy difference of particles within each cluster type. (c) Deviation of bond lengths between particles in each cluster type $\bar{r}_{ij}^C$ from the mean bond length $\bar{r}_{ij}$. 
crystal. Similarly 5A and 6A are part of the ground state HCP crystal structure. The 5A cluster and other clusters found in trace quantities are not part of the ground state FCC crystal structure. These clusters arise due to thermal fluctuations of the particle positions creating transient bonds between particles that do not exist in the ground state. The 9X cluster is an example of this phenomenon for the HCP phase.

For the BCC crystal phase 5A, 6A and 9X are structures that are found universally throughout the phase as these are part of the ground state crystal structure. Quantities of FCC and HCP are identified along with trace amounts of the other clusters due to thermal fluctuations.

For the liquid phase the 5A structure is most frequently seen and other structures are found in varying quantities. There are trace amounts of FCC and HCP crystalline order, and the 13A icosahedron is the least frequently seen structure. This result is contrary to Frank’s original hypothesis [35] and has been shown in earlier studies [84–87]. The particles within 9X structural environments are found in the liquid phase, confirming the statement in section 3.7.9 that this cluster cannot be used to uniquely distinguish crystalline order. Other clusters are seen in various quantities.

In figure 3.40(b) the difference in potential energy between particles identified within each cluster type and the all-particle average is shown. The energy $U_C$ is the total potential energy of all $N_C$ particles identified within a certain cluster type, such that $U_C/N_C$ is the mean potential energy of each membering particle. Comparison is drawn with $U/N$ the mean potential energy of all particles.

For the FCC and HCP phases the formation of any structural order not found in the ground state crystal by thermal fluctuations is associated with an increase in potential energy for those participating particles. Trace amounts of FCC order are seen in the HCP phase and, although the FCC crystal is the free energy minimum phase for this state point [88], the increase in potential energy arises due to the interfacial energy penalty of the boundary introduced between the two crystalline structures.

For the BCC phase the formation of clusters not associated with either BCC, FCC or HCP crystalline order results in an increase in potential energy for the participating particles. When FCC and HCP order is formed the participating particles see a drop in potential energy. This result is an indication of the greater stability of the FCC and HCP phases even at the expense of introducing an interface.

The order that is found in the liquid phase results in a drop in potential energy for
the participating particles. The exception is for the 5A structure where $N_{5A}/N \approx 1$ as the difference in potential energy must be close to zero. There is a moderate anti-correlation between $N_{C}/N$ and the drop in potential energy for the ground state clusters (5A to 13A).

Figure 3.40(c) displays the effect of participating in clusters on the local packing of particles. The length $\bar{r}_{ij}$ is the mean bond length of the neighbour network, and $\bar{r}_{ij}^{C}$ is the mean length of bonds between particles participating in a particular structure type. The difference $\bar{r}_{ij}^{C} - \bar{r}_{ij}$ indicates the change in bond lengths for particles forming a particular structural order.

The FCC and HCP phases show an increase in bond lengths for structures not associated with the pure crystalline order for each phase. This result implies that the formation of any non-crystalline order is associated with local fluctuations of the density. As the mean bond length in uniform systems is proportional to $\rho^{-1/3}$ to a good approximation, the magnitude of any density fluctuation is necessarily small due to the low relative fluctuations in the mean length between the regions of different structure.

For the BCC phase the formation of clusters associated with FCC and HCP order results in a local increase in density, and there is a local decrease for any other found that is not associated with any of the crystalline orders.

For the liquid phase only very small changes in the mean bond lengths are seen on formation of the ground state clusters 5A to 13A. Again this indicates that the formation of this order is not associated with any local fluctuations in density, but instead caused by different orientational arrangements of the particles being explored. There is an increase in local density on formation of FCC and HCP clusters, however the magnitude of the increase is small compared to the difference in densities of the liquid and crystalline phases at this state point.

For completeness figures 3.41 and 3.42 contain detection results for all the other structures that are included in the TCC algorithm within the four LJ phases. The results are broadly similar to those described above for the ground state clusters and the FCC, HCP and 9X clusters.

### 3.8. Summary and discussion

In this chapter we have reviewed a number of methods for measuring higher-order correlations of particle density than are captured at the level of pair-correlation functions.
Figure 3.41: Detection of the other $m = 6$ to 10 particle clusters with the TCC algorithm. Bond detection method is modified Voronoi with $f_c = 0.82$. 
Figure 3.42: Detection of the other $m = 11$ to 13 particle clusters with the TCC algorithm. Bond detection method is modified Voronoi with $f_c = 0.82$. 

(a) $N_{C\cdot N}$

(b) $U_{C\cdot N} - U_{N}$

(c) $\vec{n}_{ij} - \vec{n}_{ij}$
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The reliance of these higher-order methods on a bond network as an input was emphasised, and we discussed the various strengths of three different methods for identifying the bonds: using simple cut-off length, a Voronoi tessellation, and the modified Voronoi method of Williams.

The latter part of the chapter was dedicated to the TCC algorithm. First, the algorithm was described and its implementation discussed. Second, the method was tested on LJ FCC and HCP crystal phases where known local structure was subject to distortion by thermal fluctuations. The test then proceeded to a supercooled liquid phase, where it was identified that particles align into structures with topologies similar to that of a number of ground state clusters for the LJ and other models. The particles that participate in these structures were found to reduce their potential energy by doing so, and that this occurred not due to density fluctuations but to due to their local changes in arrangement.

In the following chapter the TCC algorithm is used to study the self-assembly of colloidal clusters.
3.9. Bibliography


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CHAPTER 4

The Self-assembly of Colloidal Clusters

4.1. Introduction

In this chapter we study the structural behaviour of colloidal clusters. Colloidal clusters are locally dense packings of a small number of colloids that are readily accessible in experiments. Clusters are a distinct state of matter that exhibit a range of structural ordering, dynamics and state behaviour not seen in bulk materials [1]. Clusters are of particular relevance to nanotechnologies and the biology of viruses. Viral capsids, formed by the self-assembly of proteins, take shapes such as icosahedra and dodecahedra, which are also seen in nanoclusters [2].

Recently there has been a surge of interest in colloidal clusters [3–16] that is attributable to advances in particle synthesis. It is now possible to synthesise colloids with a wide variety of shapes, sizes and aspect ratios. This has resulted in an explosion in the variety and diversity of products that can be formed through self-assembly. It is expected that some of these structures will find a place in novel nanotechnologies due to their peculiar optical and electronic properties. It is also envisaged that nanomachines will be designed to self-assemble from simple nanoscale components and find uses in biotechnologies to engineering [17].

It is expected that studies on colloidal clusters will lead to advances in fundamental research [11]. For example, the study of ‘colloidal molecules’ could reveal details of atomic-level processes. The advantages of using colloidal clusters as pseudo-molecules is it that the timescales for their fastest motions, e.g. vibrations and rearrangements, are on the order of milliseconds, hence readily accessible in experiments, and that the larger particles (>~ 1 μm) are visible with conventional light microscopy.

Self-assembly is defined as the autonomous organisation of components into structures, due to the local interactions between the components, and without external di-
rection [17]. In principle colloidal dispersions are rather complex multicomponent systems, but the large size asymmetry between colloidal particles and smaller molecular and ionic species has led to schemes where the smaller components are formally integrated out [18]. This leads to a one-component picture where only the effective pairwise interactions between colloids need to be considered. Although this is usually a good approximation, it has been challenged, in particular with relation to non-additivity of electrostatic interactions [19] or the incorporation of electro-hydrodynamic interactions [20, 21]. Here we employ the effective one-component picture in our simulations of colloidal self-assembly.

The effective interactions that bind colloidal clusters together can arise in a number of ways. It is common to introduce a depletant into the solvent so that an entropically-driven attraction will form between the colloids [22]. This depletion interaction can be tuned for different strengths by varying the concentration of the depletant.

It is also possible to chemically pattern the surface of colloidal particles to create bonding sites, or to functionalise the colloids with molecules such as DNA to create bridging interactions. If the colloids are subject to an external field, as is the case in optical trapping experiments, they can also be brought together under the influence of the external field.

Here we are interested in the clusters formed by spherical colloids with competing short-range depletion attractions and long-range screened Coulomb repulsions, commonly known as either Yukawa [23] or Derjaguin-Landau-Verwey-Overbeek (DLVO) repulsions [24, 25]. Previous experimental and simulation studies on similar systems have seen a range of interesting behaviours from self-assembly processes. These include Bernal spirals [7, 26], novel diffusion of clusters [15], lamellae [27], and gels [28–31].

Since colloids may be directly imaged at the single-particle level, one may consider local intra-cluster structure, along with cluster-cluster correlations, at a level of detail seldom accessible in atomic and molecular systems, except in the low-temperature regime [32]. The behaviour of colloidal clusters, for example the global energy minimum structures, exhibit similarities to that of clusters of Noble gas atoms. This is because both colloids and Noble gases can be well described by spherically symmetric attractive interactions [33, 34]. The structures are also similar [34–36], although not identical [33, 35], to the structure of clusters from simple liquid models.

Here we study the self-assembly processes for a model colloidal system using Brownian dynamics (BD) simulations. The motivation for this work is to understand how the yield of a self-assembled product depends on the strength of the attractive interactions between the colloids, and of the repulsive interactions opposing assembly. The questions we address are:

1. Which clusters form through self-assembly?
2. Can the clusters that self-assemble be predicted from the ground state clusters of the interaction potential?

3. Under what interaction conditions is the yield of free energy minimum clusters maximised?

4. Under what circumstances is self-assembly to the free energy minimum state frustrated by kinetic effects?

5. What is the effect of long-range electrostatic interactions on the structure of the clusters?

6. How do electrostatic interactions between clusters affect the intra-cluster structure?

The simulations are designed to closely mimic some recent colloidal experiments [37] by matching parameters for the strengths of the interactions and the timescales of the dynamics. The simulations, like the experiments, are initialised with the colloids in a random state and are subsequently allowed to assemble on a typical timescale of a few hours. We follow this approach as it closely matches the experimental scenario, although we note recent work highlighting the importance of microscopic reversibility in optimising yields from self-assembly processes [17, 38, 39], which is now beginning to be exploited in the nanoscience field [40].

Dissimilar from the normal scenario in molecular systems, the temperature is not varied in the colloidal systems. The colloidal system undergoes an ‘instantaneous quench’ from the initial state. The effective temperature is the control parameter and this is determined by the strength of the interactions.

The simulation results will be used to predict the yields of different clusters as a function of interaction strength. This will enable direct comparison with the experimental results, where the yield of free energy minimum clusters is significantly lower than is expected [37]. In our approach we consider clusters of \( m = 3, 4, 5, 6 \) and 7 colloids, and study the structures formed, paying particular reference to the ground state clusters of the interaction potential, as identified by the topological cluster classification (TCC) algorithm [33, 34].

For sufficiently high attraction strengths (low effective temperatures) it is inevitable that the structure of the ground state clusters will coincide with the free energy minimum clusters, as the entropic contributions to the free energy become dwarfed by the interaction energy. This implies that the clusters that are formed at high attraction strengths will be the ground state clusters if the system is at thermodynamic equilibrium. However, the average bond lifetime may exceed the simulation run time for sufficiently strong interactions. The simulations are thus non-ergodic on these timescales and kinetic trapping may become important.
For intermediary attraction strengths, entropic contributions to the free energy cannot be dismissed. Particular attention is paid to the $m = 6$ case where entropic contributions determine the most popular structure of the cluster between two candidates (6A and 6Z) with similar ground state interaction energies [41].

Initially the simulations contain small numbers of particles so that the assembly process can be studied in isolation. After analysing this case, we investigate the effect of electrostatic repulsions between clusters on the intra-cluster structure using simulations containing an ensemble of clusters. This scenario mimics the experimental set-up in reference [37].

This chapter is therefore divided into two parts: first we consider the ideal case of the self-assembly in small, isolated, systems. For each cluster size, we execute long simulations of only a few colloids to generate statistics on the clusters that form. By adjusting the strength of the attractive interaction (adding more depletant polymer in the experiments) and the electrostatic repulsions, we elucidate behaviour of the self-assembly process under different conditions, section 4.2.

In the second part we simulate large systems more akin to the actual experimental set up, section 4.3. From these we numerically trace out state diagrams for regions in which (meta-)stable small clusters form as a function of attractive and repulsive interaction strengths, and colloidal volume fraction. We turn our attention to the effect of electrostatic inter-cluster interactions on the structure of the clusters that form.

In section 4.4 the relevance of the simulation results to experiments on colloidal self-assembly are discussed. A summary of the findings on colloidal self-assembly is found at the end of the chapter, section 4.5.

Note that throughout this chapter we draw comparisons between the structure of clusters that are formed through self-assembly in the thermal systems, i.e. our simulations or the experiments of reference [37], and the arrangements of $m$ particles that minimise the interaction potential when $T = 0$. At equilibrium the clusters formed in the thermal system minimise the free energy, and are termed the ‘free energy minimum’ clusters. Conversely the energy minimum $T = 0$ clusters are termed the ‘ground state clusters’ or ‘ground state structures’.

4.2. Geometric frustration in small colloidal clusters

In this section we consider the simplest case of an isolated system of a small number of particles which undergoes self-assembly to form clusters. This allows us to identify the types of clusters that might form in the experimental system [37], and how these clusters are related to the ground state clusters of the interaction potential. We also consider the effects of kinetics on the self-assembly process and how electrostatic repulsions affect the
Chapter 4. The Self-assembly of Colloidal Clusters

4.2.1. Model

In the experimental system we seek to model, van der Waals attractions are largely absent due to solvent-colloid refractive index matching. The attractions are driven by the addition of non-absorbing polymer, described by the seminal theory of colloid-polymer mixtures by Asakura and Oosawa [22]. The Asakura-Oosawa (AO) model ascribes an effective pair interaction between two colloidal hard spheres in a solution of ideal polymers. For small polymer-colloid size ratios, the AO model has been found to give good agreement with direct experimental measurement of the colloidal interactions using confocal microscopy [42].

The discontinuity in the AO interaction at contact complicates its use in Brownian dynamics simulations [43]. We therefore substitute the AO potential for the continuous Morse potential, as for short interaction ranges both potentials are similar [44].

The experimental system of reference [37] that we compare with uses a polymer-colloid size ratio of \( q = 0.225 \). This maps to a Morse range parameter \( \rho_0 = 33.06 \) for a well depth \( \beta \varepsilon_M = 6 \) according to the Noro-Frenkel extended law of corresponding states [45]. Details of the mapping between the potentials is given in appendix B.

As discussed in chapter 3, the global energy minimum structures for clusters interacting via the Morse interaction have previously been identified [33, 46]. However, to our knowledge there are no published results for the Morse potential with interaction yield of clusters.

Figure 4.1: The interactions between the colloids. (a) The Morse potential mapped to an AO potential relevant to experimental systems, using the extended law of corresponding states. (b) The competing interactions used in this study, \( \beta u_M + \beta u_Y \), for various values of the Morse potential well depth \( \beta \varepsilon_M \). The case of \( \beta \varepsilon_M = 0 \) is the pure Yukawa interaction with a contact potential of \( \beta \varepsilon_Y = 1 \) and inverse Debye screening length \( \kappa = 0.5 \).
ranges are short as $\rho_0 = 33.06$. Therefore we calculate the ground state clusters for the $\rho_0 = 33.06$ case using the publicly available GMIN optimisation package\(^1\).

The effect of decreasing the range of the potential is to increase the multiplicity of minima in the potential energy surface and to increase the heights of the barriers between the minima. Therefore careful sampling with GMIN is necessary to ensure the global minimum of the potential energy surface is sampled. This is achieved by sampling a range of temperatures and Monte Carlo (MC) step sizes in the GMIN package, until configurations that maximise the number bonds between particles are identified. It is found that for clusters with $m < 8$ particles the structure of the global energy minima at $\rho_0 = 33.06$ are identical to the published structures for $\rho_0 < 25$ [33]. These ‘ground-state’ clusters are namely 3A, 4A, 5A, 6A, and 7A.

Repulsions between the colloidal particles stem from the electrostatic charges on the surface of the particles. Often under conditions where there is weak charging, counter ions in the solution lead to a screened Coulomb, or Yukawa potential at long-ranges. To model these interactions the Debye length is fixed to an experimentally relevant value $\kappa = 0.5$, and different values of the contact potential $\beta\varepsilon_Y$ are considered. The interactions between the colloids are shown in figure 4.1.

We investigate the structure of the colloidal clusters that form using the TCC algorithm, which identifies structures equivalent to those of the ground state clusters for the Morse potential. Although we do not calculate the effect of electrostatic repulsions on the structure of the ground states, we expect that for weak repulsions the ground states for $m < 8$ are the same [34].

### 4.2.2. Simulation details

The simulation technique is BD in the $NVT$-ensemble, as described in chapter 2. The colloids respond to the direct interactions and to solvent-induced thermal fluctuations, which are treated as Gaussian noise with variance chosen in accordance with the fluctuation-dissipation theorem.

In the simulations $m$ particles are initialised randomly in a cubic box with periodic boundary conditions (PBCs) at volume fraction $\phi = m(\pi \sigma^3/6)/L^3 = 0.0029$. During the simulation we consider only the cases where all particles are part of a single cluster, defined as when each particle is connected to all the others by traversing bonds between the particles. The inter-particle interactions are truncated and shifted (i.e. $u_{TS}^{M/Y}(r_{tr})$) for $r_{tr} > 3$. This rather short value for the Yukawa potential enables the particles to form clusters more readily starting from the initial randomised state. While the Yukawa repulsion has not fully decayed at $r = 3$, the largest separation of two particle centres that we are

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\(^1\)See references [47, 48] for details of the package.
interested in is set by the size of the clusters, and for the \( m < 8 \) ground state clusters this is less than 3.

The timescale for the simulation is set by the diffusion rate of the colloids. The Stokes-Einstein equation relates the diffusion constant for a colloid to its size, the thermal energy and the dynamic viscosity \( \eta \) of the solvent:

\[
D = \frac{k_B T}{3\pi \eta \sigma}.
\]  

This formula applies for spherical particles diffusing through a low Reynolds number fluid. The typical experimental values of \( T = 298 \text{ K}, \eta = 0.00205 \text{ Pa s} \) and \( \sigma = 0.2 \text{ \mu m} \) [37] set \( D \), which is the single parameter that couples the simulation dynamics to the experiments. The diffusion constant sets the timescale for the colloidal diffusion in the limit of infinite dilution. We define the Brownian time as the time taken for a colloid to diffuse its own radius:

\[
\tau_B = \frac{(\sigma/2)^2}{6D}.
\]

In the experiments \( \tau_B = 1.5 \text{ s} \), which in the simulations corresponds to \( \tau_B = 711 \) reduced time units.

The timestep is \( \delta t = 0.03 \). All runs are equilibrated for \( 10^9 \) steps and run for further \( 10^9 \) steps. The rather long simulation runs were required to be sure that, in the case of Yukawa repulsions, the particles had ample time to interact with one another and form clusters. The simulation runs therefore correspond to a total of around 35 hours, a timescale certainly comparable to the experimental work. The results for each state point are averaged over between four to twelve statistically independent simulation runs.

For analysis with the TCC algorithm two particles are identified as bonded using the simple cut-off method with \( r_c = 1.25 \), which is close to the attractive range of the AO potential. The ground state clusters for the Morse potential with range \( \rho_0 = 33.06 \) are 3A, 4A, 5A, 6A, and 7A for \( m = 3, 4, 5, 6 \) and 7. However we also search for clusters corresponding to ground states of other potentials, and a range of clusters that are not ground states of an interaction potential but instead are statistically relevant configurations for some state points\(^2\).

### 4.2.3. Results

Each cluster size is considered in turn before drawing together all the results. The yields of clusters are studied as a function of two parameters: the well depth of the attractive

\(^2\)Note that the ground state clusters for the Kob-Andersen (KA) and Wahnström clusters were not included in this study as their detection routines were added to the TCC algorithm after this work was completed.
Morse interaction $\beta \varepsilon_M$, and the contact potential of the Yukawa repulsion $\beta \varepsilon_Y$. Increasing $\beta \varepsilon_M$ promotes clustering, while increasing $\beta \varepsilon_Y$ acts to suppress clustering. In experiments on colloids the electrostatic charge is usually not systematically varied, therefore we consider specific values of $\beta \varepsilon_Y$ and plot the response of the system to $\beta \varepsilon_M$.

We find that small clusters with $m \leq 5$ are able to reach the free energy minimum structures (which maximise the number of bonds). For larger clusters, under certain conditions geometric frustration leads to kinetic trapping, which severely limits the yield of the free energy minimum clusters. Here geometric frustration means that the colloids in one cluster are unable to rearrange into the structure of a cluster with lower (potential or free) energy without having to cross an energy barrier.

**Small clusters $m \leq 5$**

In figure 4.2(a) we consider the case of $m = 3$ particles. The main conclusion from these data, as with all cases where $m \leq 5$, is that increasing the attractive interaction strength $\beta \varepsilon_M$ leads to a higher population in the free energy minimum structure, which is identical to the Morse potential ground state structure. For $m = 3$ this is the ‘3A’ triangle with $D_{3h}$ point group symmetry and three bonds.

The yield of each type of cluster is measured by the fraction of all three particle clusters with that structure, written $N_C/N_m$. Note that this quantity is equal to the fraction of all particles detected within a specific three membered cluster, i.e. $N_C/N_m$, as only configurations where all particles participate in a size $m$ cluster are considered.

The high yields of 3A upon increasing the attraction strengths occur at the expense of higher energy clusters, which for $m = 3$ are ‘linear’ clusters with two bonds. In the case of $\beta \varepsilon_Y = 0$ the potential energy for a short-range interaction such as the $\rho_0 = 33.06$ Morse potential is approximately equal to the number of bonds. Since 3A triangles have three bonds, and the linear clusters have only two, the gain in potential energy of the 3A cluster as the attractions are increased will eventually dominate the decrease in entropy by forming the 3A cluster. At lower interaction strengths, however, the yields of 3A and linear clusters are comparable as both the energetic and entropic contributions make significant contributions to the free energy.

Figure 4.2(b) shows the effect of increasing the Yukawa repulsion. The effect is to slightly suppress the development of the 3A population, as is expected for the competing interactions in this system. The slight upwards shift in the potential $\beta u_M + \beta u_Y$ (figure 4.1(b)) due to the Yukawa contribution perturbs the $m = 3$ system.

Although not shown in figure 4.2, it was found that $\beta \varepsilon_Y = 5$ substantially suppressed the colloidal aggregation and few three-membered clusters were formed. Therefore strong long range repulsions can stabilise the system in a metastable gaseous state. Hereafter we only consider the $\beta \varepsilon_Y = 0, 1, 3$ cases where cluster formation is always seen.
Figure 4.2: (a) Cluster populations for the $m = 3$ system as a function of the well depth of the attractive interaction $\beta \varepsilon_M$, with $\beta \varepsilon_Y = 0$. Here we define cluster population by the ratio $\mathcal{N}_C/\mathcal{N}_m$, where $\mathcal{N}_C$ is the total number of clusters of a particular type and $\mathcal{N}_m$ is the total number of $m$ membered clusters identified. We see a clear trend towards the 3A triangle as the free energy minimum structure. The orange line corresponds to $\tau_L = 1000 \tau_B$, our criterion for ergodicity being broken (see (c)). (b) Population of clusters with the ground state structure of the Morse potential (3A triangle) for different strengths of the Yukawa interaction $\beta \varepsilon_Y$. The principal effect of the Yukawa repulsion is to shift the curves to require higher values of $\beta \varepsilon_M$ to achieve the same population of clusters in the ground state. (c) The average bond lifetime $\tau_L$ as a function of $\beta \varepsilon_M$ for various $\beta \varepsilon_Y$ as indicated. The orange lines correspond to $\tau_L = 1000 \tau_B$. (d) The linear→3A transition can be accomplished by rotating one end particle around the central particle. This pathway involves no energetic penalty for $\beta \varepsilon_Y = 0$. Error bars on all graphs are two standard deviations in length.
The average bond lifetime $\tau_L$ is shown in figure 4.2(c). We define bond lifetime as the time between a bond forming (where the separation between two colloids falls below $r_c = 1.25$) and a bond breaking (where the separation between the same two colloids rises above 1.25). The bond lifetimes were widely distributed in all cases. For $\beta \varepsilon_M \lesssim 10$, $\tau_L$ is very much less than the simulation length ($\approx 4 \times 10^4 \tau_B$), so the system may be regarded as ergodic. In this regime, $\tau_L$ exhibits an Arrhenius-like behaviour, as expected for an equilibrated system.

At higher values of the interaction strength, the average bond lifetime approaches the simulation run time and the system may fail to equilibrate. The system is regarded as non-ergodic on these timescales as it does not explore all possible configurations. We employ a bond lifetime of $\tau_L = 1000 \tau_B$ to demark the crossover between ergodic and non-ergodic behaviour.

The ergodic to non-ergodic transition is indicated with an orange line in figure 4.2(a). Although the system is non-ergodic for high attraction strengths ($\beta \varepsilon_M \geq 10$), the absence of any geometric frustration enables the free energy minimum state to be reached.

The absence of geometric frustration is understood as follows (figure 4.2(d)): for $m = 3$, if $\beta \varepsilon_Y = 0$ there is no energy barrier in the linear $\rightarrow$ 3A cluster transition. In other words, a steepest descent quench in the potential energy landscape for a three-membered cluster will always result in the 3A triangle.

Turning to the case for $m = 4$ colloids, the situation is more complex (figure 4.3(a)).
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Figure 4.4: Cluster populations for the $m = 5$ system as a function of the well depth of the attractive interaction $\beta \varepsilon_M$, with $\beta \varepsilon_Y = 0$. The orange line corresponds to $\tau_L = 1000 \tau_B$. Error bars are two standard deviations in length.

Rather than two states as for $m = 3$, there are five structures that we distinguish: 4A tetrahedra (the ground state with 6 bonds and $T_h$ point group symmetry) and diamonds (5 bonds), triangle-lines and squares (4 bonds), and linear clusters (3 bonds). Squares are distinct from diamonds in that there are no diagonal bonds between the particles.

For low $\beta \varepsilon_M$, the most popular configurations of $m = 3$ clusters are linear, triangle-line and diamond clusters. Each higher energy state has a distribution which becomes progressively less favoured at higher values of $\beta \varepsilon_M$. The 4A becomes the dominant structure with a yield that approaches unity for $\beta \varepsilon_M \gtrsim 10$. Akin to the $m = 3$ case, there are no energy barriers in the kinetic transitions between other $m = 4$ clusters into the 4A cluster, i.e. there is no geometric frustration.

Squares have a rather low yield, much less than triangle-lines (3A+1), which have the same number of bonds. This is likely because squares have lower entropy than triangle-line states. We return to the case of competing structures during our analysis of $m = 6$ particle clusters.

The effect of increasing the Yukawa interaction is similar to the $m = 3$ case: the development of the 4A population is somewhat suppressed (figure 4.3(b)). It has been suggested that the introduction of repulsions might be expected to promote more elongated structures [49]. For a given strength of the attractive interactions $\beta \varepsilon_M$, there is indeed a tendency towards a higher population of the elongated 4D diamond structure, however the overall trend towards favouring the ground state cluster is unaltered. Henceforth we restrict our analysis to the $\beta \varepsilon_Y = 0$ case for the larger clusters.

The $m = 5$ system for $\beta \varepsilon_Y = 0$ is shown in figure 4.4. We find that for $\beta \varepsilon_M \gtrsim 8$, the overwhelming majority of clusters adopt the ground state structure 5A (triangular bipyramid
with 9 bonds and $D_{3h}$ point group symmetry). Defective triangular bipyramids ($4A+1$) form an excited state with 10 or 11 bonds. Clusters based around 4-membered rings with 5-8 bonds ($sp4b$ and squares+1) are present in yields up to a few percent for relatively weak attractions ($\beta \varepsilon_M \sim 5$). Five-membered rings (pentagons, five bonds) are found in small quantities, similar to the square in the case of $m = 4$.

The main result from considering these small clusters is that, although the system may become non-ergodic on the simulation timescale, the clusters can nevertheless access the free energy minimum structure for large interaction strengths ($\beta \varepsilon_M \gtrsim 8$). For $m = 3$, 4 and 5 clusters there are no energy barriers that have to be crossed in order to transform into the ground state structure. This statement is equivalent to saying there is no possibility for kinetic trapping in the potential energy landscape.

For $m = 5$ we have not explicitly considered all possible structures. For example linear clusters may form at weaker interaction strengths. At $\beta \varepsilon_M = 4.5$ only around 10% of the $m = 5$ clusters are identified, however for most interaction strengths we consider, the vast majority of clusters have one of the five structures considered. It is also true that at higher interaction strengths our analysis identifies the dominant structures for $m = 6$ and 7 particle clusters.

$m = 6$ clusters: competing structures

For $3 \leq m \leq 5$ the free energy minimum structure at high interaction strengths is the global energy minimum cluster of the Morse interaction. However in the case of $m = 6$, 

Figure 4.5: (a) Cluster populations for the $m = 6$ system as a function of the well depth of the attractive interaction $\beta \varepsilon_M$, with $\beta \varepsilon_Y = 0$. Error bars are two standard deviations in length. Here at strong interaction strengths rather than the Morse ground state 6A octahedron, 6Z clusters are found. The 6Z clusters are the ground state clusters for the Dzugutov potential, shown in (b). The orange line corresponds to $\tau_L = 1000 \tau_B$. (c) The $3A \rightarrow 4A \rightarrow 5A \rightarrow 6Z$ aggregation pathway with does not involve the breaking of any bonds and thus promotes the formation of 6Z over 6A for high values of $\beta \varepsilon_M$. 

for 6Z over 6A for high values of $\beta \varepsilon_M$. 

with 9 bonds and $D_{3h}$ point group symmetry). Defective triangular bipyramids ($4A+1$) form an excited state with 10 or 11 bonds. Clusters based around 4-membered rings with 5-8 bonds ($sp4b$ and squares+1) are present in yields up to a few percent for relatively weak attractions ($\beta \varepsilon_M \sim 5$). Five-membered rings (pentagons, five bonds) are found in small quantities, similar to the square in the case of $m = 4$.

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this is not the case (figure 4.5(a)). We see only a small population of the Morse global energy minimum, the 6A octahedron ($O_h$ point group symmetry), with another structure of $C_{2v}$ point group symmetry appearing to dominate the yield. This cluster is the ground state for the Dzugutov potential (plotted in figure 4.5(b)) [50], and it is known as the 6Z cluster.

Why should the yield of Dzugutov 6Z clusters be higher than the 6A octahedra? Both clusters have 12 bonds (near-neighbours), and for a Morse potential with a relatively short range as we use here, the energy contribution from second-nearest neighbours is a factor of $5.65 \times 10^{-7}$ of the total energy for the 6A cluster (it is almost zero for 6Z). In fact, when the Yukawa repulsions are added, 6Z becomes energetically favoured as it is more elongated. Let us first consider the case for neutral particles where $\beta \epsilon_Y = 0$.

The difference between the two clusters’ ground state potential energies is slight, but the entropic contributions to the free energy need to be considered to determine which cluster is the most stable for ergodic state points. To this end we calculate the relative number of states that the 6A and 6Z clusters contribute to the partition function. The partition function is calculated as the product of three approximately independent terms representing the translational, vibrational and rotational freedom of the clusters. The details of this calculation are given in appendix C, and we find 6Z thermodynamically favoured over 6A by a factor of 23. This result is close to the simulation result for $N_{6Z}/N_{6A}$ across all state points where both clusters are formed with significant yields (figure 4.5(a)).

As $\beta \epsilon_M$ becomes very large, we would ultimately expect a trend towards a 6A dominated population due to the (small) differences in the potential energy. However, on these simulation timescales, the average bond lifetime is too long to enable the transition to a 6A dominated population due to kinetic trapping. The 6Z cluster is the result of a $3A \rightarrow 4A \rightarrow 5A \rightarrow 6Z$ aggregation sequence (figure 4.5(c)), so tends to form first from the random initial configuration, in preference to 6A. The conversion of 6Z into 6A requires bond breakage, and at strong interaction strengths this is improbable for kinetic reasons.

Like the smaller clusters, for $m = 6$ we identify different structures which are significant for lower values of $\beta \epsilon_M$. In decreasing yield, these are clusters with two tetrahedra (which we denote as $5A+1$ in figure 4.5(a), with either 10 or 11 bonds), defective octahedra (denoted as $sp4b+1$, with between 9 and 11 bonds), defective pentagonal bipyramids (denoted as $sp5b$ with 10 bonds) and clusters formed of a five-membered ring with one bound particle (pentagon+1, between 6 and 9 bonds).

$m = 7$ clusters: kinetic trapping

For the small clusters we have considered so far, the number of particles is too small for the system to become trapped in metastable states under thermal conditions. However,
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Figure 4.6: Cluster populations for the $m = 7$ system as a function of the well depth of the attractive interaction $\beta \varepsilon_M$, with $\beta \varepsilon_Y = 0$. Here the Morse ground state 7A pentagonal bipyramid is readily formed at intermediate interaction strengths. The orange line corresponds to $\tau_L = 1000 \tau_B$. A cluster based on three overlapping 5A triangular bipyramids, $3 \times 5A$, shows a re-entrant behaviour, dominating the cluster population at high and low values of $\beta \varepsilon_M$. Error bars are two standard deviations in length.

for $m = 7$ we see that the yield of the Morse global energy minimum 7A pentagonal bipyramid approaches unity for moderate strengths of $\beta \varepsilon_M$, but for $\beta \varepsilon_M > 12$ not all simulations reach the 7A ground state structure (figure 4.6(a)). This is caused by kinetic trapping in a higher energy state.

Once the 7A is formed at high attraction strengths the system remains in a 7A state as it minimises the free energy. However if other metastable states are formed before 7A, the system may become kinetically trapped if the bond lifetimes are very large. The rise in 7A population as a function of $\beta \varepsilon_M$ appears to slow around the ergodic to non-ergodic transition (defined as $\tau_L = 1000 \tau_B$).

In the non-ergodic regime bond breaking governs the structures that form and up to $m = 6$ we expect an aggregation sequence similar to the $3A \rightarrow 4A \rightarrow 5A \rightarrow 6Z$ sequence shown in figure 4.5(c). Stepwise aggregation of one particle onto a 6Z cluster is likely to lead to a structure we term $3 \times 5A$, decomposed into 3 overlapping 5A triangular bipyramids, or equivalently a 6Z cluster with an additional tetrahedron, rather than 7A. This is because there is a larger surface area of the 6Z cluster where an extra particle could adhere a $3 \times 5A$ would result, compared to the surface area that would yield a 7A cluster.

The $3 \times 5A$ structure has 15 bonds, while the 7A has 15 bonds where the particle separation is unity (i.e. the minimum of the Morse potential) plus an additional contribution from the interaction between the two spindles particles. The separation between the spindles is 1.02 and the interaction between these particles contributes $0.447 \varepsilon_M$ to the energy. The 7A ground state cluster is thus lower in energy than the $3 \times 5A$ structure.
At low interaction strengths the $3 \times 5A$ structure is favoured over $7A$ due to its larger entropic contribution to the free energy. In the non-ergodic regime we see that this $3 \times 5A$ structure displays a re-entrant behaviour, and at $\beta \epsilon_M = 14.5$ no $7A$ clusters are seen at all. The behaviour of the $7A$ system in the non-ergodic regime highlights the sampling limitations of our simulation approach. To map the thermodynamic equilibrium behaviour of this regime more accurately, longer simulations or the use of rare-event sampling techniques would be required.

At weaker interaction strengths, like for the smaller clusters, a variety of structures are seen based on a diminishing number of bonds. Of these, $sp5b+1$, a defective pentagonal bipyramid with 11-13 bonds shows a rather slow rate of decay upon increasing $\beta \epsilon_M$. Clusters with fewer bonds tend to be promoted for weak interaction strengths by entropy, while in the non-ergodic regime kinetic trapping favours $3 \times 5A$ due to the aggregation sequence.

4.2.4. Discussion

The behaviour of the isolated clusters is readily split into cases where kinetic trapping is not possible, i.e. $m \leq 5$, where a well-defined structure is favoured, and cases where kinetic trapping limits access to the ground state structure in the limit of high attraction strengths, $m \geq 6$.

In the case of $m = 6$ two structures with the same number of bonds, $6A$ octahedron and $6Z$ $D_{3h}$, compete. The difference in ground state energies of these two clusters is very small, so the equilibrium thermal behaviour is determined by entropic contributions to the free energy. This scenario demonstrates that it is incorrect to assume that the ground state cluster will also be the free energy minimum structure under thermal conditions with moderate attraction strengths. At large attraction strengths $6Z$ clusters dominate the structures seen, and kinetic trapping prevents the $6A$ configurations from being explored.

For $m = 7$ and moderate attraction strengths the ground state cluster is the free energy minimum cluster ($7A$). At high attraction strengths a higher energy state ($3 \times 6Z$) displays a reentrant behaviour and is favoured over $7A$. This is because the normal aggregation sequence from the initial configuration results in $3 \times 6Z$ rather than $7A$, and the system becomes kinetically trapped in the $3 \times 6Z$ state.

Of particular relevance here is the short range of the attractive interactions. It has been noted previously that short range attractions promote a complex energy landscape with more minima and larger energy barriers between them [2]. For example $m = 13$ Morse clusters with $\rho_0 = 14.0$ have some 54439 local energy minima, compared to just 685 for the longer-ranged case of $\rho_0 = 4.0$ [51]. The Morse potential with $\rho_0 = 14.0$ is an approximation to $C_{60}$, clusters of which are known to exhibit kinetic trapping [52].
our system $\rho_0 = 33.06$ and stronger trapping is expected.

### 4.3. The effect of inter-cluster interactions on the intra-cluster structure

Having considered a small number of colloidal particles in isolation and the clusters that are formed, we proceed to model an ensemble of clusters that are stabilised by long-range electrostatic repulsions. This state is known as a cluster fluid [5, 7].

Colloidal cluster fluids are found in systems with competing interactions of short-ranged attractions and long-ranged repulsions [5, 7]. The attractions drive clustering while the repulsions prevent aggregation and phase separation. The clusters formed have a characteristic size [49]. At sufficient concentration these cluster fluids percolate and form gels [7, 26, 29, 30], while for sufficiently strong repulsions the cluster fluid can undergo dynamical arrest [31, 53] or crystallisation [54].

The separation in length and time-scales allows us to treat a cluster fluid in a hierarchical manner. For example, dynamical arrest (kinetic trapping) within clusters and dynamical arrest of a fluid comprised of clusters [31, 53] can in theory be decoupled. Indeed it has been suggested that one may consider each cluster as an isolated system [37].

Here instead we consider the influence of the inter-cluster interactions on the intra-cluster structural behaviour. In other words how is the free energy landscape of an isolated cluster perturbed by the presence of neighbouring clusters?

In the experimental study of a cluster fluid by Klix et al. [37] it was observed that there was a particularly low yield of 4A tetrahedra compared to diamond structures under conditions where the free energy minimum structure (4A) is attained in the $m = 4$ isolated simulations above. The inclusion of inter-cluster interactions in the simulations below will determine if the repulsions between clusters are a factor in this discrepancy.

As before the simulations are characterised by the colloid packing fraction $\phi$, the strength of the attractive interaction $\beta\varepsilon_M$, and the strength of the repulsion $\beta\varepsilon_Y$. We first determine the range of parameters that correspond to a cluster fluid state, before investigating the effect that varying these parameters has on the intra-cluster structure.

#### 4.3.1. Simulation details for interacting clusters

We consider $N = 1000$ particles for the following state points: $\beta\varepsilon_Y = \{1, 3\}$, $\phi = \{0.02, 0.05, 0.10\}$ and $\beta\varepsilon_M = \{5, 6, 7, 8, 9, 10, 11, 12\}$. These parameters span monomer fluid, cluster fluid, and aggregates/gel states. The sampling for each state point consists of 8 statistically independent simulations. Particles are initialised randomly subject to a non-overlap constraint within the cubic box. PBCs are implemented.
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Figure 4.7: Snapshots of the three states seen in the simulations. (a) $\beta \varepsilon_Y = 3, \phi = 0.02$, $\beta \varepsilon_M = 5$: monomer fluid where more than 50% of the particles are identified as monomers/unbonded, (b) $\beta \varepsilon_Y = 3, \phi = 0.02$, $\beta \varepsilon_M = 9$: cluster fluid in which we are interested, (c) $\beta \varepsilon_Y = 1, \phi = 0.10$, $\beta \varepsilon_M = 12$: aggregate/gel where more than 50% of particles are identified in $m > 10$ clusters.

The potentials are truncated and shifted at different lengths compared to the simulations of the isolated clusters. For the simulations of the interacting clusters the cut-off length for the Morse potential is $r_{tr} = 1.5$ where it is typically less than $10^{-6}$. The Yukawa repulsions are truncated and shifted for $r_{tr} = 10.175$, where the potential is of the order $10^{-3}$. Ewald summation methods exist to calculate the long-range, slowly decaying, component of Yukawa interactions from the periodic images of the simulation box [55]. However the Ewald methods are not used here as the Debye length $\kappa = 0.5$ means that we are far from the Coulomb limit.

As the Brownian time is $\tau_B \approx 711$ time units, and these larger simulations are equilibrated for $1.5 \times 10^7$ steps and run for $1 \times 10^7$ steps, the simulations correspond to approximately 1000 Brownian times or around 25 minutes of experimental time. This timescale is comparable to the experimental work [37].

We study the evolution of the system as the particles condense into small clusters under the influence of the Morse attractions. The clusters are stabilised against bulk phase separation by the long-range Yukawa repulsions. The structure of the clusters that form are identified with the TCC algorithm.

4.3.2. Results

State diagram

Here we are interested in metastable cluster fluids, however at low density and/or low attraction strengths the system is dominated by unbound particles in a state we term a monomer fluid (figure 4.7(a)). At high density we find aggregation into much larger and often elongated clusters, in agreement with [34, 49], and ultimately gelation (figure
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Figure 4.8: Cluster size distributions. On the horizontal axis \( m \) is number of particles in a cluster and on the vertical axis \( P(m) \) is the fraction of all clusters with \( m \) particles. The lines represent different values of \( \beta \varepsilon_M \). (a) \( \beta \varepsilon_Y = 1, \phi = 0.02 \), (b) \( \beta \varepsilon_Y = 3, \phi = 0.1 \).

4.7(c) [7, 26]. Between the aggregation/gelation regime and the monomer fluid lies the cluster fluid, figure 4.7(b).

We determine the state points that are cluster fluids numerically. We analyse the size distribution of the clusters across the state points, as shown in figure 4.8. For weakly attracting systems at low density, \( \beta \varepsilon_Y = 1, \phi = 0.02, \beta \varepsilon_M \sim 4 \), the system is dominated by monomers. There is a crossover to a system dominated by clusters at \( \beta \varepsilon_M \sim 7 \). At higher interaction strengths, the number of monomers drops markedly, as the system moves towards larger clusters.

For moderate values of the attractive interaction most clusters have a size \( m \leq 10 \), figure 4.8(a). We take an arbitrary value of 50% to distinguish the three states in figure 4.7. Systems with more than half the particles as monomers are said to be a monomer fluid, and with more than half the particles in \( m > 10 \) aggregates as either aggregated/gelled.

Increasing the colloidal packing fraction to \( \phi = 0.1 \) and the Yukawa interaction strength to \( \beta \varepsilon_Y = 3 \), figure 4.8, leads to a somewhat different scenario. Clusters are found at all measured attraction strengths. Furthermore for moderate interaction strengths the distributions are flat. No monomers or dimers are present for \( \beta \varepsilon_M > 8 \).

Finding clusters at all interaction strengths is likely due to the increase in packing fraction for \( \phi = 0.1 \). At \( \phi = 0.1 \) the mean inter-particle separation \((6\phi/\pi)^{-1/3}\) is 1.74, and the Yukawa repulsion varies only by 1.81 between a distance of 1.74 and particle contact, so its contribution is small compared to the attractive interactions. Therefore particles can readily approach each other at this state point in order to form clusters.

Based on the cluster size distributions the state diagrams in the \( \phi - \beta \varepsilon_M \) plane are plotted out using our cluster size criterion to demark the three states, figure 4.9. The generic nature is similar to that found in previous simulation studies [26] and experi-
mental work [7]. Monomer fluids exist at low density and weak attractions, gels at higher density/attractions, and cluster fluids in between. Our definitions lead to a crossover rather than an abrupt transition between monomer to cluster fluid, and cluster fluid to aggregate/gel states. The differences between figures 4.9(a) and (b) are reasonably understood in terms of the increase in Yukawa repulsion, which inhibits clustering at the low colloid packing fractions $\phi$ we consider.

**Inter-cluster interactions**

Pair correlation functions for two cluster fluids are shown in figure 4.10. Figure 4.10(a) is a low-density $\phi = 0.02$, $\beta \varepsilon_Y = 1$, $\beta \varepsilon_M = 6$ system, while figure 4.10(b) shows $\phi = 0.1$, $\beta \varepsilon_Y = 3$, $\beta \varepsilon_M = 7$.

In both cases, the intra-cluster structure for $r < 3$ shows strong peaks. The long-range behaviour of the pair correlation functions also allows us to comment on the strength of the cluster-cluster interactions. Figure 4.10(b) shows a broad peak at $r \sim 4$, whereas at longer ranges in figure 4.10(a) $g(r)$ is almost flat. The highlighted peak in figure 4.10(b) indicates that the clusters exhibit strong correlations with their neighbours, i.e. they are interacting with one another. Conversely figure 4.10(a) is a weakly interacting system.

By thinking of the cluster fluid as a fluid of (polydisperse) Yukawa-like particles [28], we can gain some idea of the interaction between clusters. For the state point in figure 4.10(b), the mean cluster size is $\langle m \rangle \approx 8.75$. Typical cluster-cluster separations are given by the cluster-cluster peak i.e. $r_{CC} \sim 4$. If we consider clusters of average size at the typical separation, we have a total cluster-cluster interaction (i.e. the total interaction energy
Figure 4.10: Pair correlation functions in cluster fluids. (a) Weakly interacting cluster fluid, \( \phi = 0.02, \beta\varepsilon_Y = 1, \beta\varepsilon_M = 6 \). (b) Strongly interacting cluster fluid, \( \phi = 0.1, \beta\varepsilon_Y = 3, \beta\varepsilon_M = 7 \).

Conversely in the case of figure 4.10(a) there is a very weak peak around \( r \approx 6.25 \), \( \langle m \rangle \approx 3.55 \), which leads to a typical total cluster-cluster interaction strength of \( \beta u_{CC} \approx 0.15 \). We can thus speak of weakly interacting (figure 4.10(a)) and strongly interacting (figure 4.10(b)) cluster fluids. We expect that the clusters in a weakly interacting cluster fluid will show little change relative to isolated clusters, but that in a strongly interacting cluster fluid, the energy landscape of each cluster can be perturbed by its neighbours.

**Cluster populations**

In the cluster fluid we identify the structure of each cluster individually using the TCC algorithm. The number of clusters of each type are normalised by the total number of clusters of \( m \) particles, i.e. \( N_C / N_m \). If there is no effect of inter-cluster interactions on the intra-cluster structure, it is expected that the results should be identical to what was found in the simulations of isolated clusters.

Our main results are shown in figures 4.11 and 4.12. The general trend of the results at moderate to high attraction strengths is in agreement with the yields for isolated clusters. For example, the 3A triangle, 4A tetrahedron, 5A pentagonal bipyramid and 6Z are the most frequently occurring structures at \( \beta\varepsilon_M \approx 9 \) for all densities. These are the free energy minimum clusters in isolation, as shown by the green lines that reproduce the data for the simulations of isolated clusters with \( \beta\varepsilon_Y = 1, 3 \).

For \( m = 6 \) particle clusters, figures 4.11(d)(e) and 4.12(d)(e), the 6Z \( C_{2v} \) and the 6A \( O_h \) structures compete. Both have the same number of near-neighbours, but the inclusion of Yukawa repulsions means that 6Z is favoured energetically as the structure is more...
Figure 4.11: Cluster populations of each cluster size $3 \leq m \leq 7$ as a function of the well depth of the attractive interaction $\beta \epsilon_M$. Here we fix $\beta \epsilon_Y = 3$. Symbols denote the colloid packing fraction: isolated clusters for $\beta \epsilon_Y = 3$, diamonds; $\phi = 0.02$, circles; $\phi = 0.05$, triangles; $\phi = 0.1$, squares. The different plots correspond to various clusters: (a) 3A $D_{3h}$ triangles, (b) 4A $T_d$ tetrahedra, (c) 5A $D_{3h}$ triangular bipyramids, (d) 6A $O_h$ octahedra, (e) 6Z $C_{2v}$, and (f) 7A $D_{5h}$ pentagonal bipyramids.
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Figure 4.12: Cluster populations for $\beta \varepsilon_Y = 1$. Symbols refer to colloid packing fraction: isolated clusters for $\beta \varepsilon_Y = 1$, diamonds; $\phi = 0.02$, circles; $\phi = 0.05$, triangles; $\phi = 0.1$, squares. The different plots correspond to clusters: (a) $3A D_{3h}$ triangles, (b) $4A T_d$ tetrahedra, (c) $5A D_{3h}$ triangular bipyramids, (d) $6A O_h$ octahedra, (e) $6Z C_{2v}$, and (f) $7A D_{5h}$ pentagonal bipyramids.
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elongated than 6A. As discussed in the section on isolated clusters, 6Z is also heavily favoured due to entropy.

In the case of 7-membered clusters (figure 4.11(f)), the population of the global minimum 7A \( D_{5h} \) pentagonal bipyramid does not tend to unity. We showed that this is due to ergodicity breaking at relatively deep quenches, such that geometric frustration can prevent access to the pentagonal bipyramid ground state [56]. For these relatively short simulation runs (total length is \( 400\tau_B \)), once the attractive interaction strength exceeds \( \beta \varepsilon_M \sim 5.0 \) the bond lifetime exceeds the simulation run time.

For moderate attraction strengths it may be the case that the more elongated \( 3 \times 6Z \) structure has lower free energy than the 7A structure as the difference in energy of the ground states will be reduced due to the Yukawa repulsions between the particles. This interpretation is consistent with the fact that the yield of 7A clusters decreases as \( \beta \varepsilon_Y \) increases (comparing figure 4.12(f) to figure 4.11(f)), although this may also be attributable to kinetic effects.

We now turn our attention to the role of increasing density for the \( \beta \varepsilon_Y = 3 \) system, figure 4.11. We see a general trend of higher density promoting access to the free energy minimum clusters. The effect of colloid packing fraction is strongest around \( \beta \varepsilon_M \sim 6.0 \). For example, we find an order of magnitude increase in the 6Z population at \( \beta \varepsilon_M = 6 \) upon increasing the packing fraction from \( \phi = 0.05 \) to \( \phi = 0.1 \) (figure 4.11(e)). The effect of raising the colloid concentration may thus be thought of as acting in a similar way to an increase in attraction \( \beta \varepsilon_M \).

The 6A octahedron population is around 1/30 that of the 6Z, which is consistent with the simulations of isolated clusters and with some experiments on isolated clusters [41]. Compared to isolated systems we see rather more 7A pentagonal bipyramids at low attraction strengths, indicating that the repulsions are stabilising the more compact \( m = 7 \) states.

In the case of weaker Yukawa repulsions (figure 4.12), our arguments above concerning ‘strongly’ and ‘weakly’ interacting cluster fluids would lead us to believe that reducing the repulsions would lead to weaker inter-cluster interactions and less perturbation of the intra-cluster behaviour. This interpretation appears to be valid: compared to figure 4.11, the relatively weakly interacting clusters in figure 4.12 show less response to increasing the colloid packing fraction.

In particular the more dilute \( \phi = 0.02 \) and 0.05 show little deviation from one another, and are in good agreement to the isolated cluster data for \( \beta \varepsilon_M \geq 6.5 \). This suggests that for these parameters, the cluster fluid approaches the dilute limit and behaves as a ‘cluster gas’. Note that the experimental system considered in [37] was close to \( \phi = 0.02, \beta \varepsilon_Y = 1 \), i.e. it is ‘weakly interacting’.

Interestingly for \( m = 7 \) there is a smooth decrease in the yield of 7A clusters for \( \beta \varepsilon_M \geq \)
8 when $\phi = 0.02$ and 0.05, figure 4.12(f). The isolated cluster data do not show such a trend. The decrease in yield in the cluster fluids is explained by kinetic trapping. As the simulations of cluster fluids are much shorter than the isolated cluster simulations there is less time for $3\times6Z$ clusters to rearrange to the 7A configuration.

4.3.3. Discussion

We have considered the effect of cluster-cluster interactions on the intra-cluster structure of model colloidal clusters in a cluster fluid. The overall behaviour is broadly similar to the behaviour of isolated clusters. That is to say, upon increasing the strength of the attractions clusters are able to attain their free energy minimum structures.

For weak cluster-cluster interactions, $\beta\varepsilon_Y = 1$, the intra-cluster behaviour depends little upon density, and only shows deviation from the isolated cluster behaviour at weak attraction strengths. Therefore the interacting clusters may reasonably be treated as independent systems for this repulsion strength.

Upon increasing the electrostatic repulsions between the clusters, $\beta\varepsilon_Y = 3$, a more marked effect of cluster-cluster interactions is seen. For attractive interaction strengths where there is a competition between different structures due entropic effects, increasing density and consequently the relative strength or inter-cluster interactions results in more clusters being identified in the energy minimum states (3A, 4A, 6Z, 7A). In other words the energy landscape of each cluster is perturbed by its neighbours.

This may be qualitatively understood in terms of the repulsive Yukawa interactions between clusters. The pair repulsion energy between clusters typically increases as the clusters approach one another upon raising the colloid packing fraction. The inter-cluster repulsions might be expected to lead to more ‘compact’ clusters, in order to minimise the repulsive interaction strength. One example of ‘compact’ is a cluster which minimises its radius of gyration. For spheres, these are 3A triangles, 4A tetrahedra, 5A triangular bipyramid, 6A octahedra and 7A pentagonal bipyramids [57].

This conjecture is true for 3A, 4A, 5A and 7A, but the $m = 6$ case is a special case. The 6Z energy minimum cluster is favoured over the 6A compact cluster for all attraction strengths and packing fractions due to entropic and energetic reasons (6Z is lower in energy than 6A with the inclusion of Yukawa repulsions). However the effect of increasing density also results in an increase in yield of 6A clusters at moderate attraction strengths, at the expense of more elongated clusters than 6A and 6Z.

An interesting approach to test this conclusion would be to take a system which forms markedly different clusters, such as ‘patchy particles’, which can be tailored to form less compact structures in the ground state [13]. The competition between compact clusters favoured by density and the less compact ground state clusters could then be investigated.
It is important to note that, although we simulate on experimentally relevant timescales, the cluster fluids we have studied here may not be truly at equilibrium. Colloidal cluster systems have been shown in simulation to form cluster crystals [54] or lanes [58], but this suggests a more uniform cluster size distribution than we find here. Therefore, even though our cluster-cluster interactions can reach $14k_B T$, the polydispersity of the system prevents crystallisation.

Systems with competing interactions often exhibit some form of structural ordering [59]. It is reasonable to suppose that much longer simulation runs than we have been able to perform here might result in a shift in the cluster size distribution to one which is more monodisperse. Moreover, state points at higher concentration might be expected to develop into columnar phases or lamellae with a clear periodicity [27, 59]. We have not investigated the cluster dynamics in this system, but it is possible that there is a cluster glass region of the state diagram.

According to the definitions we have used here, there is no sharp transition between cluster fluids and aggregates/gels. Increasing density/attractions leads to aggregation and gelation. Locally in the gel we may expect the structure to resemble that of the clusters. This situation was seen in experiments on gelation without long-ranged repulsion [44]. With competing interactions, as is the case here, a crossover from a cluster glassy state to a gel has been seen [53], where gelation is interpreted as a percolation phenomenon. That study found little change in local structure upon gelation. Thus both arrested spinodal type gels without long-ranged repulsions [44, 60], and gels resulting from percolation in a system with competing interactions [7, 30, 53] may have a local structure dominated by a topology which follows that of isolated clusters.

### 4.4. Relevance to experiments

This simulation work was motivated by experimental studies of clustering in colloidal dispersions. In the experimental systems the attractions, either Asakura-Oosawa or van der Waals, are typically rather short ranged, and thus likely to exhibit kinetic trapping similar to the systems studied here. We therefore argue that for substantial yields of more complex ‘colloidal molecules’, it is appropriate to seek more sophisticated means than the spherically symmetric spheres we have considered here, such as patchy particles [8, 11, 14, 40, 61] and Janus particles [62, 63], or to design routes of preparation [4, 64]. However, even ‘purpose-designed’ patchy particles can have only a rather limited window of attraction strengths where the yield of ground state structures is substantial [13, 65, 66].

We now compare our results to those found in an experimental system in which the interactions are, to a first approximation, identical [37]. Each of the isolated simulations
was conducted with a fixed number of particles corresponding to the cluster size investigated. By contrast, most experiments are carried out with a bulk colloidal suspension, in which clusters of different size form, akin to our larger simulations. The experimental data report the relative abundance of cluster types for a fixed number of particles per cluster, \( m \), and each cluster is assumed to interact only weakly with other clusters. The assumption of weakly interacting clusters is supported by our results on inter-cluster interactions.

In the experimental system, \( m = 3 \) formed a majority of clusters in the 3A triangle which maximises the number of bonds. This occurred at interaction strengths comparable to those where triangles are found in our simulations. In the experiments \( m = 4 \) and 5 formed only around 10% of 4A tetrahedra and 5A triangular bipyramids respectively, in sharp contrast to our simulation results, where the yield is essentially 100%. In the case of \( m = 6 \), both in experiment and simulation, the yield of 6Z \( C_{2v} \) dominated the yield of 6A octahedra. However, in ergodic simulations, the population difference was around a factor of 30, while in the experiments the difference was at least an order of magnitude larger. Furthermore, the maximum yield of 6Z \( C_{2v} \) was an order of magnitude lower in the experiments than the simulations where it is around 100%. For \( m = 7 \) both experiments and simulations show signs of geometric frustration, with the yield of 7A being reduced in the nonergodic regime of strong attraction strengths. However, while the peak yield of 7A approached 100% in the simulations, in the experiments the yields were limited to a few percent of 7A.

Here we discuss possible origins for the discrepancy between our simulation results and those of reference [37]. In reference [37] it is suggested that kinetic trapping in meta-stable \( m = 4, 5, 6, \) and 7 states is due to an anisotropic self-organised surface charge distribution. It is argued that the surface charging on the colloids in anisotropic and this prevents colloids rotating around each other to reach lower potential energy states. Another plausible scenario is that chemical bridging interactions between the colloids leads to anisotropic interactions and suppression of cluster rearrangements.

### 4.5. Conclusions

We have studied the self-assembly of colloidal clusters using Brownian dynamics simulations. By employing the TCC algorithm we were able to automate the identification of the structure of self-assembled clusters. We were thus able to map out the structures that form as a function of attraction strength, repulsive interaction strength, and interactions between clusters (set by \( \phi \)).

The results for \( m = 6 \) at \( \beta \varepsilon_T = 0 \) demonstrated that the free energy minimum clusters are not identical to the ground state clusters. Here 6Z is higher in energy than 6A, but
favoured by a factor of $> 20$ due to entropic contributions to the free energy. We also learned that for $m = 7$, the system can become kinetically trapped in a higher energy states (e.g. $3 \times 6Z$) due to the aggregation sequence of 7 colloids from a random initial configuration, and the long lifetime of the bonds at high attraction strengths. For clusters with $m = 3$ to 5 colloids, kinetic trapping was not seen and, for moderate to high attraction strengths, the structures of the free energy minimum states coincide with the structures of the ground state clusters.

For the isolated clusters the effect of electrostatic repulsions between the particles was to shift the attraction strengths required to form clusters by the contact Yukawa potential. The addition of Yukawa repulsions also resulted in the $6Z$ cluster becoming energetically favoured over the $6A$ cluster.

The effect of interactions between clusters mediated by Yukawa repulsions was evaluated in simulations of an ensemble of clusters. We considered two methods for varying the strength of the inter-cluster interactions: by varying $\beta \varepsilon_Y$ or $\phi$. For large values of $\beta \varepsilon_Y$ and $\phi$ the yield of clusters was perturbed compared to the case of isolated clusters. In each case the inter-cluster interactions promoted the yield of compact clusters, which coincide with the lowest free energy clusters.

Recent experimental results show much lower yields of clusters that our simulations infer are the free energy minimum states [37]. The origin of the discrepancy is likely to be related to a difference in the effective interactions between the experiments and the simulations. In future it may be appropriate to move beyond the one-component description for the attractions employed here to better understand self-assembly in colloidal experiments.

It is perhaps surprising that such small systems exhibit this degree of kinetic trapping; it was only for small cluster sizes, $m = 3$, 4, and 5, for which there is no geometric frustration that kinetic trapping is not seen. This result suggests that high yields of complex micro-structures of colloidal clusters and molecules may benefit from reversible quenching [17, 38–40], rather than the fixed interactions of many colloidal systems, which lead to ‘instantaneous quenching’.
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4.6. Bibliography


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5.1. Introduction

In this chapter we address the structure in the interfacial region between a coexisting liquid and gas. In the late 19th century Rayleigh and van der Waals described the liquid-gas interface with a smooth density profile $\rho(z)$ perpendicular to the interface that decreases monotonically from the liquid to the gas [1–3]. Subsequent theoretical work based on the Born-Green-Yvon equation by Croxton suggested that surface layering should exist in van der Waals liquids [4], and this was indeed seen in computational studies of two dimensional Lennard-Jones (LJ) interfaces [5]. However, simulations in three dimensions failed to find any layering [6], and density functional theories predicted that there is no layering in 3D van der Waals systems [3, 7]. The interfacial density profile in 3D LJ systems is a monotonic function as Rayleigh suggested.

Metals typically remain liquid to lower temperatures relative to the critical temperature $T_c$ than van der Waals systems. Surface layering at metallic liquid-gas interfaces in three dimensions is predicted by density functional theory and indeed found in simulations [7–11].

A related problem to the free interface is that of a liquid under confinement by a hard wall, crystal or similar external field. Confinement problems have been studied with density functional theory [7, 12], simulations [13] and experiments [14–16]. Layering is more generally observed for liquids under confinement than for free liquid-gas interfaces. The structure at the interface of a liquid confined by hard walls has been shown to be characterised by five-fold symmetries in the local particle structure [16, 17].

For the free interface the measurement of intrinsic interfacial density profiles in experiments on atomic and molecular systems is complicated by collective surface excitations known as capillary waves [18–21]. For systems where surface layering is pronounced, such as metals, the lengthscale above which capillary wave effects become
dominant is around 100 nm. This lengthscale is larger than what is typically accessed in computational studies, where capillary waves only cause a small broadening of the surface layering and can often be neglected [9]. Although the effect of capillary waves on the density profile cannot be neglected in experiments, some studies have demonstrated surface layering at free interfaces, for example in liquid mercury [22].

Another class of experiments used to study liquid-vapour interfaces are colloidal dispersions. The constituent particles in these systems are often visible in real space, so the study of the interface is greatly simplified. Moreover the simple hard-sphere like interactions that approximate the colloidal interactions are more amenable to theory than atomic and molecular interactions [23].

In colloid-polymer mixtures the colloids separate into high and low density fluid phases [24, 25] and capillary waves have been visualised directly [26]. To our knowledge, interfaces in colloidal systems with long-ranged interactions [27] that can be cooled deeply with respect to the critical point and are expected to exhibit pronounced layering (equivalent to metals) have yet to be studied. The unwanted effects of capillary waves in such systems can be removed by pinning a plane to a layer of surface particles from which the density profile perpendicular to the interface is measured [28]. This method was used in a study of critical behaviour in colloid-polymer mixtures and indeed revealed density oscillations perpendicular to the surface [29].

In this chapter we consider the perturbation of the liquid structure at local level that is induced by the interface. We consider two different systems with phase coexistence: (i) a LJ system [30, 31], and in order to observe stronger effects of the interface (ii) a model for sodium introduced by Chacón-Reinaldo-Falagán-Velasco-Tarazona (CRVT) [8, 10], where the interface can be stabilised at lower temperatures relative to the critical point.

The maximum degree of cooling for the LJ free interface lies at $T_{LJ}^{tr}/T_{LJ}^{c} = 0.630$, where $T_{LJ}^{tr}$ is the triple point and $T_{LJ}^{c}$ is the critical temperature. This compares to a lower value $T_{CRVT}^{tr}/T_{CRVT}^{c} = 0.22$ for the sodium model. The liquid-gas interface in the CRVT model is known to exhibit strong surface layering around the triple point, a result which is supported by ab initio simulations of liquid sodium interfaces [11].

In order to measure the perturbation that the interface induces on the liquid structure, we measure the frequencies that particles participate in small clusters in the vicinity of the interface. The clusters that are analysed are equivalent in structure to the clusters that minimise the potential energy of 5 to 13 particles interacting in isolation. The results of the analysis reveal that the clusters seen in the bulk liquid are suppressed towards the free interface. For state points where interfacial layering is seen the density profiles of the clustered particles tend to follow the oscillations in the bulk density.

Some of the clusters identified are anisotropic as their length is greater than their
width or breadth. Two commonly found anisotropic clusters are the 5A triangular bipyramid and 7A pentagonal bipyramid. These clusters are found to order orientationally at the interface, with their longest dimensions lying parallel to the interface.

5.2. Methodology

5.2.1. Models and simulation details

The Monte Carlo (MC) method is used to simulate liquids in equilibrium with their vapour phases [32]. The first system is single component LJ, which is a model for the van der Waals interactions between argon atoms (chapter 2). We employ truncated and shifted potential in the simulations, with \( r_{tr} = 2.5 \). The critical temperature under this truncation scheme is \( T_{c}^{LJ} = 1.0795 \) [31] and the triple point is estimated to be near \( T_{tr}^{LJ} = 0.68 \) [33]. Therefore, the maximum degree of cooling relative to the critical point is \( T_{tr}^{LJ}/T_{c}^{LJ} = 0.630 \).

To realise lower temperature liquid-vapour interfaces relative to the critical temperature, we simulate a metallic system. In particular, we employ the spherically symmetric model for sodium introduced by Chacón et al. [8, 10], here given the acronym CRVT. The CRVT potential is rescaled such that its minimum lies at the length of the minimum of the LJ potential, namely \( 2^{1/6} \), and the depth of the attractive well is unity. Following reference [10], the potential is truncated but not shifted at a length \( r_{tr} = 2.5\sigma_0 \), where \( \sigma_0 \) is given by \( u_{CRVT} (\sigma_0) = 0 \). This allows us to take the literature values of the triple point, estimated at \( T_{tr}^{CRVT} = 0.27 \) and critical point, around \( T_{c}^{CRVT} = 1.25 \) [10]. This model enables much lower temperatures relative to the critical point to be realised. For the sodium

![Figure 5.1: Pairwise potentials: LJ, black line; re-scaled CRVT, red line.](image-url)
model $T_{tr}^{CRVT} / T_c^{CRVT} = 0.22$. In figure 5.1 we plot the LJ potential and the rescaled CRVT potential.

Results are presented at two state points for each model. In the case of the LJ model these are $\rho = 0.32, T = 0.95$ and $\rho = 0.32, T = 0.68$. For the CRVT model we have $\rho = 0.485, T = 0.542$ and $\rho = 0.485, T = 0.297$. These points correspond to $T / T_c = 0.880, 0.630, 0.434$ and $0.237$, where $T_c$ is the critical point of the LJ or CRVT models respectively.

The MC simulations sample configurations from the $NVT$ ensemble and consist of $N = 16000$ particles. The simulation box is a cuboid with side lengths $L \times L \times 2L$ and periodic boundary conditions (PBCs). This geometry ensures that once equilibrated the liquid forms a slab with two interfaces to the vapour that lie perpendicular to the $z$-direction. Assuming the interface does not overlap with itself, the $z$-position of the top or bottom interface may be expressed as a function of $(x, y)$. The cuboid side length is $L = 29.2$ for the LJ state points and $L = 25.5$ for the CRVT state points.

For all simulations suitable liquid-vapour coexistence initial configurations are generated by first estimating appropriate bulk liquid $\rho_L$ and vapour $\rho_G$ densities at coexistence from the literature [8, 34]. A slab of liquid at density $\rho_L$ is then equilibrated in coexistence with a vapour at $\rho_G$ for at least 300000 MC sweeps.

It has been shown that the coexistence densities and $\rho(z)$ depend on the system size, the geometry of the box, and the boundary conditions of the simulation [35], as well as the truncation details for the potential [34]. Thorough equilibration of our samples is ensured by checking for relaxation of the total potential energy and examining the evolution of the liquid-vapour density profile $\rho(z)$; once the density profile $\rho(z)$ is seen to have stopped evolving, we say the system has equilibrated.

A production run of 10000 MC sweeps is used to generate 100 independent configurations for analysis. The $z$-coordinates of the particles are rescaled such that the centre of mass of the particles in the $z$-direction is zero. The cuboid is then split at $z = 0$ into two cubes each containing a single interface. For the lower cube the $z$ to $-z$ coordinate transformed is performed so the geometry matches that of the upper cube. At least four independent simulations are performed for each state point so that the results are averaged over at least eight liquid-vapour interfaces.

### 5.2.2. Determining the interface location

To determine the location of the interface we fit the density profile $\rho(z)$ with a hyperbolic tangent function

$$\rho(z) = \frac{\rho_L + \rho_G}{2} + \frac{\rho_L - \rho_G}{2} \tanh \left( \frac{z - z_0}{w} \right), \quad (5.1)$$

where $w$ is the width of the interface. This function provides a smooth transition from liquid to vapour densities at the interface.
Figure 5.2: Identification of the position of a capillary perturbed interface. The interface is shown in blue and the cube is split into $n^2$ columns, each of which is indexed by integers $i$ and $j$ denoting position along the $x$- and $y$-axes respectively. The interface is assumed to be flat within each column such that the position can be extracted by fitting the step function (equation (5.2)) to the columnar density profile $\rho_{i,j}(z)$. Periodic boundaries exist in the $x$ and $y$ directions only.

where $w$ quantifies the width of the interfacial region and $z_0$ is the position of the interface with respect to the $z$-axis. As discussed below, $w$ as determined by equation 5.1 cannot account for the broadening effect of capillary waves on the interface. It is difficult to accurately decouple the intrinsic width of the interface from that of a capillary broadened interface [35]. The position of the interface extracted with equation 5.1 is found to be sufficient for our purposes however.

To assess the effect of capillary waves, the interfacial width is decomposed into capillary-broadened $w_{cw}$ and intrinsic components $w_{int}$, such that $w = w_{cw} + w_{int}$ [36]. The effect of surface roughening due to capillary waves is determined as follows [37]. Firstly we divide the simulation cube into $n^2$ columns of width and breadth $L/n$ and height $L$, as shown in figure 5.2. The density profile $\rho_{i,j}(z)$ in each column $(i,j)$ is modelled with a step function

$$\rho_{\text{step}}(z) = \begin{cases} 
\rho_L & z < z_{0,i,j}, \\
\rho_G & z \geq z_{0,i,j},
\end{cases}$$

where $z_{0,i,j}$ is the position of the interface, and $i$ and $j$ index the columns. We minimise the least square residuals between $\rho_{i,j}(z)$ and $\rho_{\text{step}}(z)$ to find $z_{0,i,j}$.

Re-scaling the $z$ axis in each column as $z - z_{0,i,j}$ gives columnar density profiles cen-
tred on the position of the interface. Taking the mean of these columnar profiles gives \( \rho_{av}(z) \), the averaged density profile with capillary waves at and above the columnar scale removed. The averaged density profile is then fitted with the hyperbolic tangent function of equation 5.1 yielding a new interfacial width \( w_n \). Due to capillary broadening, the square of \( w_n \) has a logarithmic dependence on the column width [36]. Extrapolating the column width to zero gives an estimate of the intrinsic interfacial width.

For the \( \text{LJ} \ T = 0.95 \) state point, capillary waves make the largest contribution \( w_{cw} \). The minimum interfacial width obtained by this procedure is \( w_n = 2.11(1) \), compared to a width of \( w = 2.38(2) \) obtained without treatment for the capillary waves. The difference is only around 10% of \( w_n \) obtained, hence we conclude that capillary roughening of the interface is minimal for all the state points we consider for simulations of this size. Hereafter we neglect the effect of capillary waves and fit the density profiles of each interface with equation 5.1 to determine \( z_0 \). We henceforth shift the \( z \)-axis in each cube such that \( z_0 = 0 \), and measure clustering of the particles with respect to the interface.

### 5.2.3. Structural analysis

The topological cluster classification (TCC) algorithm is used to analyse the structure in the interfacial region between the liquid and the gas. The bond network is detected with the modified Voronoi method, with four-membered ring parameter \( f_c = 0.82 \) and maximum bond length \( r_c = 1.8 \).

The clusters of \( m = 5 \) to 13 particles in isolation that minimise the energy of the \( \text{LJ} \) interactions are 5A, 6A, 7A, 8B, 9B, 10B, 11C, 12B, and 13A, see figure 5.3. For the \( \text{CRVT} \) model, the ground state clusters are found using the publicly available \( \text{GMIN} \) optimisation package [38, 39]. The ground state clusters for the \( \text{CRVT} \) model are 5A, 6A, 7A, 8A, 9B, 10B, 11A, 12B and 13A, also depicted in figure 5.3.

Clusters within the bulk simulations are identified by the TCC algorithm if their structure is equivalent to one of the ground state clusters. In addition to the ground state clusters for each model, the structures based on face-centred cubic (FCC) and hexagonal close packed (HCP) thirteen particle clusters are also identified.

### 5.3. Results

We begin by showing the interfacial profiles of the different systems and state points in figure 5.4. The interfacial width drops with decreasing \( T/T_c \). The lowest temperatures, and thus the smallest interfacial widths, are realised for the model sodium system. For the lowest temperature \( \text{CRVT} \) state point there is substantial interfacial layering, as shown by the oscillations in the density of the liquid phase on approaching the interface. The layering we find is in agreement with earlier results [8, 10]. The layering density os-
Figure 5.3: The ground state clusters for the LJ and CRVT potentials and their point group symmetries.
Figure 5.4: Interfacial density profiles $\rho(z)$. From top, LJ: $T = 0.95$, $T = 0.68$, CRVT: $T = 0.542$, $T = 0.297$. The CRVT interface at the lowest temperature shows a very pronounced surface layering. Interfacial widths $w$ are quoted and the data for each state point are offset vertically for clarity.

collations extend far into the bulk liquid, indicating that the structure of the equilibrium liquid is perturbed by the presence of the interface.

We now proceed to the TCC structural analysis of the liquid and how it changes in the liquid towards interface with the gas. We plot the density of particles identified within a particular type of cluster, $\rho_C(z)$, for the ground state structures in figures 5.5(a) and (c). The clustered particle density is defined as:

$$\rho_C(z) = \lim_{\delta z \to 0} \frac{N_C(z)}{L^2 \delta z},$$

(5.3)

where $N_C(z)$ is the number of particles identified in clusters of type C within the volume element between $z$ and $z + \delta z$.

The densities are plotted as a function of the distance from the liquid-gas interface at $z = 0$. As the gas is basically devoid of structure, and our interest lies with the effect of the interface on the liquid structure, only the liquid side of the interface is plotted (i.e. $z \geq 0$).

In addition to $\rho_C(z)$, the fraction of particles identified within each type of cluster, $N_C(z)/N(z)$, is plotted as a function of $z$, figures 5.5(b) and (d). Note that this fraction is also the ratio of the clustered particle density to the overall number density, i.e. $N_C(z)/N(z) = \rho_C(z)/\rho(z)$

In the bulk liquid away from the interface it is seen that the most popular cluster is the 5A triangular bipyramid which consists of two face sharing tetrahedra. This cluster...
Figure 5.5: TCC analysis of the LJ liquid-vapour interface. The density $\rho_C(z)$ denotes the density of particles participating in clusters of a particular type. The black lines are the density profiles $\rho(z)$ (as per figure 5.4). (a) $T = 0.95 (T/T_LJ = 0.880)$. (b) Fraction of particles identified in clusters as a function of position from the interface. (c) The triple point $T_{tr} = 0.68 (T/T_LJ = 0.630)$. (d) as (b). The yellow gradient is a guide to the eye that indicates the extent of the interfacial region.
accounts for more than half of all the particles at both state points. After 5A, other clusters seen in significant quantities (> 5% of the particles) are 6A, 7A and 8B for both state points, and 9B and 10B as well for $T/T_c^{LJ} = 0.630$. Larger clusters are only seen in trace quantities.

Moving towards the interface the densities of the clustered particles decrease. The relative decreases are greater than the drop in the overall particle density, an effect most readily seen in figures 5.5(b) and (d) where the clustered particle densities are normalised by the overall density. The decreases in clustered particle densities occur within the interfacial region (shown by the yellow gradient in figure 5.5) and are most rapid at $z = 0$.

The decrease in clustered particle densities in the interfacial region reflects the transition between the structureless gas where particles are predominantly isolated to the liquid where packing effects lead to clustering. Clustering has previously been shown to result from the packing of hard spheres in bulk fluids without interfaces [40]. It may be argued that the attractions between the particles promote the formation of ground state clusters, using a purely energetic reasoning along the lines of that made by Frank for supercooled liquids in 1952 [41]. Indeed research by Taffs et al. has shown that ground state clusters are more common in an equilibrium LJ liquid than in its purely repulsive Weeks-Chandler-Andersen (WCA) interaction counterpart [42]. However it must also be noted that the same study found the converse result for Morse liquids with short-range attractions. In that case the attractions suppressed the yield of ground state clusters compared to the purely repulsive counterpart to the Morse potential. That result, and the fact that here it is shown that yield of clusters has a strong density dependence, indicate that the clustering found at the state points we consider arises predominantly because of the packing of the particles rather than the attractions between them.

Note that the triple point in general has a higher population of clusters than $T = 0.95$ does. This result is explained as the liquid has a higher density at the triple point, while the lower temperature promotes localisation of the particles and hence any effect of attractions is likely to be more relevant than for the higher temperature state point.

There is no anomalous behaviour in participation fractions for clusters containing five-fold rings of particles (7A, 8B, 9B, 10B, 11C and 13A) on approaching the interface. These clusters may be taken as a proxy for local five-fold symmetry, which is seen parallel to the interface in liquids in contact with a structured substrate [16, 17]. Indeed the rate of decrease in participation of the four-fold symmetric octahedron, 6A (green circles, figure 5.5(b)), is slightly lower than for clusters 7A and 8B at $T/T_c^{LJ} = 0.880$. This would indicate that five-fold symmetry is disproportionately suppressed compared to four-fold symmetry by the free interface. A similar effect is not seen at $T/T_c^{LJ} = 0.630$ however, where the decrease in yield of 13A icosahedra is comparable to that for four-fold crystal
clusters FCC and HCP.

To gain more insight into the effect of the interface on the cluster population, it is desirable to make the effect of the interface more pronounced by going to lower temperatures. The LJ system is unstable to crystallisation for $T < T_{LJ}^{c}/T_{LJ}^{tr} = 0.630$, therefore we study the sodium system where the liquid is stable at lower temperatures relative to the critical point.

At high temperatures the results for the sodium system are qualitatively similar to the LJ system. We therefore consider two state points, $T/T_c^{CRVT} = 0.434$ and $T/T_c^{CRVT} = 0.237$, that are at lower temperatures relative to the critical point than for the LJ system. As figure 5.4 shows the interface becomes narrower and at the lowest temperature there are oscillations of the bulk density profile indicating surface layering. The layer demonstrates that the interface can influence the structure further into the liquid than for the LJ system.

Once again we show the absolute densities for all the clusters on a logarithmic scale, and then the fraction of particles participating in clusters on a linear scale (figure 5.6). For $T/T_c^{CRVT} = 0.434$ the scenario is broadly similar to the higher temperature LJ state points. The densities for clustered particles are constant in the bulk, and begin to decrease upon entering the interfacial region. The relative decrease in clustered particle densities is greater than for the overall density. There is certainly no increase in popular-
ity of clusters containing five-fold rings owing to orientational ordering near the interface. In fact the decrease in the popularity of clusters these clusters towards the interface is larger than that which occurs for the four-fold symmetric octahedron 6A.

For \( T/T_c^{CRVT} = 0.237 \) where interfacial layering propagates into the bulk liquid, the clustered particle densities follow the oscillations of the bulk density (figure 5.6(c)). Curiously this does not affect the overall fraction of particles participating in the clusters (figure 5.6(d)). Given our previous inference that density (i.e. packing effects) determine the fraction of clustered particles, this seems like a counter-intuitive result. It is rationalised by noting that the wavelength of the density oscillations are less than one unit length, i.e. shorter than the steric bond-length \( 2^{1/6} \). The ground state clusters are elongated structures with longer lengthscales than this, therefore the particle fraction for the clusters will necessarily be constant along the density oscillations.

The exception to this argument occurs if there is a systematic drift in the density occurring over longer lengthscales across the layering region. This is seen for two peaks closest to the interface, and the result is a monotonic decrease of \( N_C(z)/N(z) \) through these density oscillations. The conclusion remains that clustering is mainly driven by packing effects and overall density. Consequently there is no anomalous behaviour in the liquid structure near the interface that is measurable in terms of the amount of clustering of the particles, other than a smooth decrease in structure as the density drops through the interfacial region.

Although the fractions of particles within clusters showed no anomalous behaviour, the interface may have an effect on the orientational ordering of the clusters. To this end we consider the alignment of clusters near to the interface. Two clusters are considered: the triangular bipyramid 5A and the pentagonal bipyramid 7A. These are 3-membered and 5-membered rings, respectively, with two spindle particles pointing out in a direction perpendicular to the ring (ignoring thermal fluctuations). The 6A octahedron based on the 4-membered ring is discounted due to its high symmetry.

To measure the orientation of these clusters relative to the interface, we consider the angle \( \theta \) between the line connecting the spindle particles and the normal plane to the interface (figure 5.7). Inspired by orientational ordering in liquid crystals, we construct an order parameter \( 1/2 < 3 \cos^2 \theta - 1 > \) that quantifies the orientation of the 5A and 7A clusters relative to the interface. In the bulk isotropic liquid all orientations have equal probability and the order parameter is zero. If the spindles of the clusters are all aligned perpendicular to the interface the order parameter is unity, while it is \(-1/2\) when the spindles of the clusters lie in parallel to the interface.

In figure 5.8 we plot the order parameter as function of \( z \), taken as the point equidistant from each spindle particle along the axis that connects them, for both 5A and 7A clusters. The two types of clusters behave in opposite ways near to the interface. While
the 7A clusters tend to be aligned with the five-membered ring parallel to the interface, the 5A clusters are aligned with its origin three-membered ring perpendicular to the interface.

The magnitude of the order parameter characterising the alignment near the interface increases as the temperature decreases. At the lowest temperature the order parameter for the 7A clusters reaches a value that is 40% of what it would be for a perfectly ordered state (1.0) with five-membered rings parallel to the interface. Likewise the order parameter for the 5A clusters is 50% of the value for a perfectly ordered state (0.5) where the origin three-membered ring is perpendicular to the interface.

The reason for this alignment can be explained by considering the elongation of the clusters and the energy cost to distorting the interface locally. Assuming that the 5A and 7A configurations in the bulk are similar in structure to the zero-temperature configurations (i.e. bond stretching/compression is minimal), arranging the clusters at $z = 0$ such that its longest dimension is perpendicular to the interface would leave particles sticking out from the free surface. For low temperatures this would be an unfavourable situation in terms of the energy required to break the surface tension. For this reason the clusters align with their shortest dimensions perpendicular to the interface, i.e. origin shortest-path rings perpendicular and parallel to the interface for 5A and 7A respectively.

The ratio of the longest to shortest dimension in the ground state sodium 5A cluster is around 6% larger than for the 7A cluster. This difference explains why a stronger alignment of the 5A clusters is seen at the interface than for 7A clusters.

Interestingly figure 5.8(c) shows that the surface layering is reflected in oscillations of the orientational ordering of the clusters. The peaks in the density profile (figure 5.4)
Figure 5.8: The ordering of the 5A and 7A clusters relative to interface, as function of the distance $z$ from the interface. (a) Lennard-Jones, $T = 0.68$, $T/T_c = 0.630$; (b) Sodium, $T = 0.542$, $T/T_c = 0.434$; (c) CRVT sodium, $T = 0.297$, $T/T_c = 0.237$. Error bars are two standard deviations in length.
correspond to peaks in the order parameter indicating that the five-membered ring in 7A is parallel to the interface. Conversely troughs in the density profile are matched with corresponding minima in the order parameter indicating that the five-membered ring is perpendicular to the interface.

The consequence of this ordering is that the 7A clusters maximise the number of particles within the cluster inside the high density ‘layers’ next to the interface, and to minimise the number of particles in the lower density regions between the layers. For the 5A clusters, although the origin shortest-path rings are perpendicular to those in the 7A clusters, the ordering across the layers achieves the same effect, i.e. to maximise the number of particles of the cluster within the layers.

Although the effect of the alignment of the clusters in the density layering near to the interface is small, it shows nonetheless that the presence of the interface induces orientational ordering in the local structure of the bulk liquid.

5.4. Conclusions

We have used the TCC algorithm to study the local structure of a liquid close to a free interface. The analysis we have performed suggests that the interface has no influence on the number of particles that form clusters within the liquid close to the interfacial region.

As the density falls between the bulk liquid and vapour within the interfacial region, there is a rapid decrease in the density of particles that participate in clusters. The rate of decrease is faster than the reduction in overall density, indicating that packing effects are more important than dispersion forces for the formation of clusters within the liquid.

Cooling to lower temperatures relative to the critical point leads to density oscillations, or surface layering, that propagates into the bulk liquid. As the wavelength of the density oscillations is shorter than the characteristic size of the clusters, the participation of particles within the liquid was unaffected by the surface layering.

Although examination of clustered particle densities and participation fractions of particles within clusters revealed that the free surface has a negligible effect on the local structure of the liquid, analysis of the cluster orientations revealed that changes in the liquid structure do occur at the interface. Close to the interface the 7A pentagonal bipyramid tends to orientate with its five-membered ring parallel to the surface. Such an alignment minimises the strain of roughening the interface locally to accommodate the cluster.

Conversely the 5A triangular bipyramid is oriented with its 3-membered ring perpendicular to the interface, again to minimise the cases where particles protrude from the interfaces. Both of these effects are strongly enhanced at lower temperature as the in-
terfacial tension increases. The conclusion drawn is that elongated clusters align parallel to interfaces in such a way to minimise surface roughening locally. It is conjectured that highly symmetric clusters, such as the 6A octahedron and the 13A icosahedron, would show negligible orientational ordering next to a free-surface.

For the state point where pronounced interfacial layering is seen, orientational ordering of the 5A and 7A clusters propagates far into the liquid. The ordering acts to maximise the particle density of the cluster within the surface layers, and to minimise the number of particles within the cluster in low density regions between layers. Therefore it has been shown that the local structure of the liquid changes orientationally to accommodate any density oscillations induced by an interface.

We identify two possible extensions of this work. In this analysis we have only considered the ground state clusters. With the TCC algorithm it is possible to identify five-fold rings of particles directly. By provision of a suitable orientational order parameter for the five-fold rings, it would be possible to calculate the number density of five-fold rings lying parallel to the interface as a function of \( z \). Such a study would confirm whether there is an excess of five-fold rings near to the interface compared to within the bulk liquid.

Previous studies have suggested that five-fold rings of particles lie parallel to interfaces with four-fold symmetric crystals \([16, 17]\). It would be interesting to consider our method of analysis on such a system, and to test at a particle-level whether the attractive surface induces the formation of five-fold symmetries parallel to the interface.
5.5. Bibliography


Chapter 5. The Structure of Liquid-Gas Interfaces


CHAPTER 6

The Dynamics of Clusters

6.1. Introduction

In the previous chapters we considered static measures of structure within a system, i.e. quantities that can be measured from a single configuration of the particle coordinates. The dynamical behaviour of any local structures identified was not given any consideration, nor was how the cluster dynamics may be related to the behaviour of the whole system. In this chapter a method is developed to study the dynamical behaviour of clusters.

There have been comparatively few investigations published into the dynamics of clusters, at least compared to the number of static methods available for detecting them (cf. review in chapter 3). Previously the effect of any local structuring of the particles upon the dynamical behaviour of a whole system has been inferred by correlating static measures for structure to macroscopic dynamical observables such as viscosity or fragility. This strategy was taken by Coslovich et al. [1, 2] who found correlations between the numbers of locally preferred structures formed on cooling and the fragility of a range of binary Lennard-Jones (LJ) supercooled liquids.

Other researchers have related structure and dynamics by monitoring the dynamics of particles that participate within a particular kind of structural environment at a single given time. Dzugutov et al. calculated the mean-square displacement (MSD) of particles initially identified within icosahedral environments and found that the initial diffusive period of these particles was retarded compared to a system-wide average [3]. Other authors have performed a similar calculation using the self-intermediate scattering function (ISF) restricted to structured particles [4]. The disadvantage of this method is that the particles are only known to be part of the chosen structural environment at a single instance in time. It is therefore difficult to infer causality of the dynamics by structure when moving forwards in time, as the initial structure under consideration may have relaxed before any unusual or interesting dynamical behaviour manifests.
It is therefore appealing to consider the dynamics of clusters as whole units, rather than the dynamics of individual particles within a particular structure. Previous studies along these lines have considered the lifetimes of clusters identified with the Voronoi face analysis (VFA) and common neighbour analysis (CNA) methods [1, 5]. The strategy adopted by Coslovich and Pastore was to calculate a time autocorrelation of a binary function that is unitary when a single particle is at the centre of a particular type of VFA cluster, or zero otherwise. The lifetimes of different clusters were then calculated from the decay of the autocorrelation of the binary function. Pedersen took a similar approach for the CNA clusters based around bonded pairs. The cluster lifetime was defined as the time difference between the first and last observations of a particular CNA bond between two uniquely labeled particles.

Both the simplicity and the limitation of these methods is that they exploit a defining feature of the cluster in order to measure the lifetime, e.g. the central particle for the VFA method or the bonded pair of CNA clusters. The methods are therefore only applicable where a suitable defining feature exists for the cluster of interest. There are a number of topological cluster classification (TCC) clusters where there is not a natural feature by which the cluster can be enumerated. Examples of such clusters include Morse 12D and 12E clusters, which are highly symmetric and have no natural central particle or root pair to base detection upon. Therefore an alternative approach is required in order to study the cluster dynamics.

The method that is developed in this chapter measures the lifetime for any type of cluster using the complete set of indices for the particles within the cluster. The lifetime is the persistence time of the cluster. A lifetime autocorrelation function is defined for each cluster type from a collection of instances of different particles adopting the particular structure. The lifetime autocorrelation function characterises the temporal stability of each type of cluster, and is used to distinguish between the stability of different clusters. The advantage of the method presented here is that it is applicable for local structures identified using any of the methods reviewed in chapter 3.

Our motivation for studying the lifetimes of clusters is to understand how local structuring of particles is related to the dynamics of a bulk system. In particular we are interested in how local structural ordering is related to certain dynamical phenomena seen in supercooled liquids, such as non-Arrhenius increases in the relaxation time and spatial heterogeneities in the dynamics.

Supercooled liquids provide our main motivation, but the chapter begins with a consideration of the dynamics of isolated colloidal clusters. Analysis of the Brownian dynamics (BD) simulations of \( m = 6 \) colloids from chapter 4 provides a simple demonstration of the method for studying the dynamics of clusters, as the yield is dominated by two types of locally favoured structure with known order and free energy (6A and 6Z). The
stability of 6A and 6Z clusters is calculated from the decay of the lifetime autocorrelation function. It is found that both clusters have similar temporal stability. This result implies that transitions between indistinguishable 6Z states, or excitations a 6Z state that do not commit to a complete transition, occur with greater frequency than 6Z to 6A transitions.

We proceed to consider the lifetimes of local structures within supercooled liquids. It is found that fluctuations of the neighbour network on sub-diffusive time-scales present significant operational issues for defining the lifetime of a cluster. Appealing to inherent structure configurations to minimise the effect of microscopic fluctuations does little to mitigate this issue. It is therefore deemed necessary to introduce a timescale by which continuous observations of a particular cluster can be joined together across periods where it goes undetected. This process yields physically relevant lifetimes for different structures within supercooled liquids.

A Wahnström LJ supercooled liquid provides the test case, and the findings from this analysis informs a more detailed study of structure and dynamics in supercooled liquids in chapter 7.

6.2. Dynamics of isolated colloidal clusters

In this section the BD simulations of \( m = 6 \) particle isolated colloidal clusters described in chapter 4 section 4.2.2 are employed. The state point is \( \beta \varepsilon_M = 10 \), without electrostatic interactions, i.e. \( \beta \varepsilon_Y = 0 \), and where 6A and 6Z structures are predominant. The 6Z structure is favoured by a factor of almost 23 over the 6A structure at this state point.

6.2.1. Distinguishing instances of a particular cluster

In order to determine the average lifetime of a particular type of cluster it is necessary to be able to distinguish individual instances of the cluster across different frames in a trajectory. For example if a 6Z cluster forms at time zero, it is necessary to have a set of rules to determine whether a 6Z cluster found at time \( t \) is the same cluster as at \( t = 0 \).

There are three factors that distinguish individual clusters. The first is the indices of the particles that form the structure. For these \( m = 6 \) simulations the indices are always \( i = 1, \ldots, 6 \), however in a bulk system with large \( N \), the cluster could consist of many different combinations of particles. It is normal practice within computer simulations that all particles are assigned unique indices, and as such it is possible to distinguish the particles within a cluster by their indices. In experiments it is not normally the case that individual particles are uniquely identifiable. For experiments on colloids and grains, however, the development of particle tracking within videos of microscopy or conventional photography data allow unique indices to be assigned to the particles. The configurational data \( r^N \) obtained therefore is in effect equivalent to what is available from
Figure 6.1: Here three 6A octahedral clusters are shown where colours are used to distinguish the particles, as indices would in simulations. Clusters (a) and (b) are indistinguishable, as (b) is a $\pi$-rotation of (a) about the axis that connects the centres of the yellow and green particles. Cluster (c) is distinguishable from (a) and (b) however. The colours red->purple->blue->orange rotate clockwise when looking from green to yellow for (c), yet rotate anti-clockwise for (a) and (b).

The second factor that distinguishes a particular structure is the type of cluster that it is detected as by the TCC algorithm. In this section we consider two possible states for a six-particle structure, either the 6A octahedron or the 6Z compound tetrahedral cluster.

The final factor that distinguishes a structure is the arrangement of the particles within the structure. The relative arrangements of the particles within a structure can distinguish two structures even if they are identified as the same TCC cluster and consist of the same particles. Two structures are indistinguishable if all the particles are the same and one structure can be transformed into the other by rotating or translating in space.

In figure 6.1 the particles within three 6A clusters are distinguished by their colour. The arrangement of the particles in clusters (a) and (b) are indistinguishable, as one cluster can be obtained from the other via a rotation through $\pi$ radians. The arrangement in (c) is distinguishable from that in (a) and (b) however, as (c) is a reflection of (b) through the plane containing the green, orange, yellow and purple particles.

The number of distinguishable states of a cluster of $m$ particles is $m!/s$, where $s$ is the symmetry number of the cluster. The symmetry number is the number of ways the cluster can be rotated through space to yield different arrangements that are equivalent to the starting configuration (as per the arrangements in figures 6.1(a) and (b)).

It is not generally the case that all of the $m!/s$ distinguishable arrangements of the particles within a cluster are differentiated by the cluster lifetime detection algorithm. This is because the number of conditions that are needed to differentiate the arrangements of
clusters with a high number of distinguishable states is large. Moreover the conditions are generally specific to each type of cluster, making practical implementation laborious.

Some conditions to differentiate the arrangement of the particles are implemented if they naturally fall out of the detection method used by the TCC algorithm. For example, the particles that form the common and distinct spindles of the 5A clusters, and the two common sp3 ring particles, in a 6Z cluster need to be explicitly differentiated in order to detect a 6Z cluster. The different types of particles are stored sequentially in a six integer array used to store the instance of the cluster. The consequence is that a spindle particle could not switch positions with one of the common sp3 ring particles in the 6Z cluster and still be detected as the same cluster. However if the two sp3 particles switch relative positions within the cluster, this scenario would not result in a new 6Z cluster being identified.

None of the arrangements of the particles in a 6A cluster are distinguished between, due to the symmetry of the cluster. The particles may switch positions within a 6A cluster freely without the rearrangements being captured by the algorithm.

In summary each instance of a cluster is differentiated by the particles indices, the type of TCC structure, and, on a case-by-case basis, the arrangement of the particles within the cluster. Each instance is given a unique id and stored in an array for that type of cluster. To speed up searching of the array of instances to determine if a cluster found at time $t$ has been detected before, the particle indices are stored (subject to separation of the different types of particle) in increasing numerical order.

### 6.2.2. The lifetime of a cluster

Now that we have defined how each instance of a cluster is differentiated by the algorithm, we can proceed to consider the lifetimes of clusters.

We initially define the lifetime of an instance of a particular cluster as the time that the instance is continuously detected between two configurations in a trajectory. If $t_{s,i}$ and $t_{e,i}$ are the initial and final times, its lifetime is

$$\tau_{\ell,i} = t_{e,i} - t_{s,i}.$$  

(6.1)

The same cluster may occur in more than one instance and have an associated lifetime for each $\tau_{\ell,1}, \tau_{\ell,2}, \ldots$. This scenario occurs if the cluster breaks up at $t_{e,1}$ in the trajectory but later reforms at $t_{s,2}$. For now we consider all of these lifetime ‘events’ as separate entities.
6.2.3. The distribution of cluster lifetimes

We consider the distribution of lifetimes for all instances of 6A and 6Z clusters in the simulations of \( m = 6 \) colloids. We define the binary function

\[
c(t) = \begin{cases} 
1 & \text{for } t \leq \tau_\ell, \\
0 & \text{for } t > \tau_\ell, 
\end{cases}
\]  

(6.2)

for an instance of a cluster. We then consider the autocorrelation of \( c(t) \) across all instances,

\[
P(\tau_\ell \geq t) = \frac{\langle c(t)c(0) \rangle}{\langle c(0)c(0) \rangle},
\]  

(6.3)

which is the fraction of the instances of a particular structure with lifetime \( \tau_\ell \) equal or greater than \( t \). The decay of \( P(\tau_\ell \geq t) \) characterises the dynamical persistence of each type of cluster.

6.2.4. Results for the \( m = 6 \) case

The lifetimes of the 6A and 6Z clusters are analysed for the BD simulation trajectories of \( m = 6 \) colloids. Configurations are saved at every 100 time units during the each trajectory and the trajectories contain 300,000 configurations in total. Twelve independent trajectories are analysed. Clusters present at the start or the end of a trajectory are discarded as their full lifetime is not known for certain.

The spacing of the configurations in the trajectories is such that the maximum displacement of a colloid between any two sequential configurations is 0.5. The advantage of this is that any rearrangement of the particles within a 6A or 6Z cluster would be associated with the break up of one instance and the formation of a new instance, even if the initial and final arrangements are not explicitly distinguished between by the algorithm. This happens because it is necessary to break a bond in order for a rearrangement to proceed, and after the bond breaks a 6A or 6Z cluster would cease to be detected by the TCC algorithm. Therefore the difficulties discussed in section 6.2.1 regarding differentiating particle arrangements within a cluster are averted, as any rearrangement to form a distinguishable state would be identified by virtue of the high resolution of the configurations in the trajectory.

In figure 6.2(a) the lifetime autocorrelation functions \( P(\tau_\ell \geq t) \) for the 6A and 6Z clusters are plotted. The trend of the data follows an exponential-like decay. This functional form is consistent with an interpretation of a constant energy barrier that must be crossed in order to rearrange a cluster, and that random thermal (Brownian) excitations are the driving force for rearrangements.

It is apparent that there are a significant fraction of the clusters (\( \approx 30\% \) in each case)
with rather short lifetimes, as indicated by the initial drop in \( P(\tau \geq t) \) for each type of cluster that does not follow the exponential fit. We explain this drop by instances of 6A or 6Z clusters that do not fully commit to the minimum of the energy landscape. These are strained 6A and 6Z that are formed instantaneously as particles undergo motion around each other between periods where the particles truly commit to 6A or 6Z states.

From the exponential fits in figure 6.2(a), a characteristic lifetime for the 6A and 6Z states is extracted. It is found that the 6Z clusters have slightly longer lifetimes on average than the 6A clusters.

In figure 6.2(b) a schematic of the transitions that may occur when an instance of either 6A or 6Z breaks up is shown. When a 6A cluster breaks up one of two things may happen: either (i) a 6A cluster forms, which could be the original 6A cluster reforming or a new arrangement forming, or (ii) a 6Z cluster is formed. We denote the fraction of times that the former scenario occurs as \( f_{AA} \) and the latter as \( f_{AZ} \). By definition one of these two scenarios must occur, hence \( f_{AA} + f_{AZ} = 1 \). For the break-up of a 6Z cluster, either a 6Z forms (\( f_{ZZ} \)) or a 6A forms (\( f_{AA} \)), and \( f_{ZZ} + f_{ZA} = 1 \).

As the rate of decay (i.e. the average lifetime) of 6A and 6Z states are approximately the same, and the 6Z states are 23 times more common than 6A states, it can inferred that 6Z to 6Z transitions are more frequent than 6Z to 6A transitions. This result follows if one assumes that \( f_{AA} = 0 \), i.e. 6A always decays into 6Z, then the equilibrium ratio of 6Z to 6A is \( 1/f_{ZA} \). In order to satisfy the equilibrium ratio of 6Z to 6A of 23, it is necessary that \( f_{ZZ} = 1 - 1/23 \approx 0.96 \) and \( f_{ZZ}/f_{ZA} = 22 \). If \( f_{AA} > 0 \) then the ratio \( f_{ZZ}/f_{ZA} \) must increase to compensate for the fact that 6A states will become more frequent, and hence it is deduced that 6Z to 6Z transitions will always be more frequent than 6Z to 6A transitions.
6.3. Dynamics of clusters in supercooled liquids

We now proceed to discuss the measurement of cluster lifetimes in supercooled liquids. We consider the Wahnström binary mixture at the state point $\rho = 1.296$, $T = 0.632$. The simulations are molecular dynamics (MD) in the NVE-ensemble, and consist of $N = 1000$ ($N_A = 500$) particles. The pair-potentials are truncated using the Stoddard-Ford method.

It has previously been identified that there is a strong increase in the number of icosahedral clusters on cooling towards the glass transition, and suggested that these clusters play an important role in determining the fragility of this mixture [1]. We therefore consider the detection of 13A icosahedra lifetimes with the dynamic TCC algorithm. Bonds are detected using the modified Voronoi method with $r_c = 2.0$ and $f_c = 0.82$. The detection of structures by the TCC is independent of the composition of the particles (A or B species) in the cluster.

6.3.1. Glassy behaviour at this state point

The glassy behaviour of the supercooled liquid at this state point is shown by the self-intermediate scattering function (ISF) [6],

$$
F_A^s(k, t) = \frac{1}{N_A} \left\langle \sum_{j=1}^{N_A} \exp[i k \cdot (r_j(t) - r_j(0))] \right\rangle.
$$

The sum extends over all of the A-species particles and $k$ is the wavevector. For supercooled liquids it is usual for the ISF to be plotted as the angular average over wavevectors.

Figure 6.3: The (a) ISF and (b) MSD for $\rho = 1.296$, $T = 0.632$ Wahnström liquid. Two trajectories are analysed: the short (blue) and long (red) trajectory. The plateau that develops at the longest times in the MSD in (b) is an artifact of the fact that particle displacements through the sides of the simulation box were not tracked.
corresponding to the first peak in the partial structure factor $S_{AA}(k_p)$, i.e. $k_p = |k_p| \approx 7.5$.

The ISF is shown in figure 6.3(a). The plateau in the ISF indicates the so-called “cage-effect” where the relaxation of a particle is inhibited due to a cage of neighbouring particles which restrict its motion through the fluid. This is called the ‘β-regime’ of the relaxation process.

The ‘β-regime’ is followed by an ‘α-regime’ where the correlation function decays to zero indicating that the liquid structure completely relaxes. The exact functional form for the ‘α-regime’ of the correlator is not known, however it is usual to fit this regime with a stretched exponential function:

$$F^A_s(k_p, t) \approx C \exp\left[-\left(t/\tau^A_\alpha\right)^{\beta}\right].$$

This is known as the Kohlrausch-Williams-Watts (KWW) functional form, where $C$, $\tau^A_\alpha$, and $\beta$ are fitted quantities [7, 8]. The α-relaxation time $\tau^A_\alpha$ quantifies the time it takes for the liquid structure to relax. The stretching exponent $\beta \leq 1$ decreases as the temperature is lowered and indicates that there is a distribution of relaxation times microscopically within the liquid. At this state point the α-relaxation time is $\tau^A_\alpha = 41$, and below we consider all timescales relative to this characteristic time.

It is also possible to consider the relaxation of a supercooled liquid with a real-space correlation function. The mean-square displacement (MSD) is

$$\langle \delta r^2(t) \rangle = \frac{1}{N} \left\langle \sum_i N \left| r_i(t) - r_i(0) \right|^2 \right\rangle.$$

This is shown in figure 6.3(b), where the different regimes of the relaxation process are demarked with orange dotted lines. In the ballistic regime $\delta r^2(t) \propto t^2$, in the caging regime sub-diffusive motion occurs, and at long times normal liquid-like diffusion is recovered, i.e. $\delta r^2(t) \propto t$.

The short trajectory consists of 3001 configurations each separated by $2.5 \times 10^{-5} \tau^A_\alpha$. The long trajectory consists of the same number of frames with a separation of $0.1 \tau^A_\alpha$ between configurations.

### 6.3.2. A first attempt at measuring icosahedra lifetimes

The lifetimes of 13A icosahedra in the short trajectory are analysed with the dynamic TCC algorithm. The method used to measure lifetimes in the first instance is as for the case of isolated colloidal clusters. Each instance of an icosahedral cluster is given a lifetime that is the time difference between the initial and final frames of a period where the cluster is continuously detected by the TCC algorithm. Icosahedra are distinguished by the indices of the 13 constituent particles, and a distinction is made as to the difference
between the ‘central’ and ‘shell’ particles. No distinction is made between the twelve shell particles (at the vertices of the icosahedron) due to the symmetry of the cluster, but the short time-spacing between configurations in the trajectory ensure that no two particles can switch position in the shell without the TCC algorithm detecting a break-up of the cluster.

In figure 6.4(a) the lifetime autocorrelation function $P(\tau^* \geq t)$ is plotted from the raw particle coordinates. Immediately a problem with the method is clear: only one quarter of the instances of icosahedra survive the ballistic regime, and no icosahedra survive the entirety of the cage-rattling regime. Why are the lifetimes of the icosahedra so short? This result is unexpected as previous studies have suggested that the icosahedral lifetimes should be commensurate with the alpha-relaxation time of the liquid [1], and that slow relaxation of icosahedra should be one component of the distributed relaxation times that set the character of the glass transition as a collective phenomenon.

The explanation is that the fluctuations of the particle positions on microscopic length-scales (i.e. sub-cage) cause bonds to break and form between neighbouring particles. The LJ potential used in the Wahnström model is softer and longer ranged than the Morse potential considered for the colloidal attractions and therefore the relative magnitudes of the fluctuations are larger in the Wahnström liquid than in the simulations of isolated colloidal clusters. The identification of a 13A icosahedron by the TCC algorithm relies on 40 bonds being in place between the 13 particles, and if any one of these bonds is absent, or if a bond instantaneously forms that is not part of the structure of the 13A cluster, then the cluster will no longer be detected.

A commonly used method to remove the effect of the microscopic fluctuations from
a set of supercooled liquid coordinates is to consider inherent structure (IS) coordinates instead. IS coordinates are obtained by minimising the potential energy of the configuration at zero temperature, in a procedure equivalent to dropping the configuration into its nearest minimum of the potential energy surface (the local minimum). The premise is that the IS configurations are the underlying configurations of the liquid with the distortion caused by the microscopic cage-rattling fluctuations removed.

In order to make the IS configurations we employ the fast inertial relaxation engine (FIRE) minimisation algorithm of reference [9]. The tuning parameters suggested in [9] are used and convergence to the IS state is accepted if the difference in potential energy between successive minimisation steps is $\Delta U/N < 10^{-5}$ and the root-mean square force $|\mathbf{F}|/(3N)^{0.5} < 0.05$.

In figure 6.4(a) the lifetime autocorrelation function as calculated from the IS configurations of the short trajectory is plotted. It is clear that employing IS configurations does not fix the issue of clusters breaking-up on ballistic timescales. As with the raw configurations, only a quarter of the 13A icosahedra have lifetimes greater than the typical timescale for ballistic motion of the particles.

We suggest that the reason for this result is because each configuration of the liquid is not well-characterised by a single IS configuration. The movement of particles within the cage mean that a number of close, but distinct, minima in the landscape are accessed by the IS configurations. These different minima possess subtly different bonding between the particles, and the differences between these bond networks cause the break-up of the 13A clusters. This interpretation is supported by the fact that the initial drop in $P(\tau_\ell \geq t)$ is greater when measured on the IS configurations than the raw configurations, indicating that the trajectory falls between different IS minima due to small ballistic changes in the particle positions.

The cluster lifetime analysis on the IS configurations is more successful in that a fraction of the 13A clusters do now possess lifetimes comparable with the cage-rattling timescale. This result demonstrates that even though in general 13A clusters do not remain intact for long periods in the IS configurations, there are regions of the IS configurations where 13A clusters do persist across the different IS minima that are accessed.

### 6.3.3. Coping with the fluctuations

In reference [5] the lifetime of CNA clusters was taken as the difference in time between the first and last configurations that an instance of a cluster was detected, irrespective of whether it was seen to break up between these configurations. We adopt this definition for a cluster lifetime and calculate $P^*(\tau_\ell \geq t)$, where the asterisk indicates the different definition for the lifetime.

A consequence of changing to this definition for the lifetime is that rearrangements of
the particles between states of a cluster that are not differentiated by the TCC algorithm, e.g. two particles switching positions in the shell of an icosahedron, will not necessarily be recorded as two different instances of 13A clusters. This is not thought to present a significant source of error in the short trajectory as the value of \( \langle \delta r^2(t) \rangle \) for the length of the trajectory is 0.056.

In figure 6.4(b) \( P^*(\tau_\ell \geq t) \) is plotted for the short trajectory. The change in definition of a cluster lifetime results in a much slower decay of the lifetime autocorrelation function. There is a relatively small decrease in \( P^*(\tau_\ell \geq t) \) across the timescale of the ballistic motion, and 85% of the 13A clusters have lifetimes greater than this timescale. A continual decrease in the autocorrelation function is seen for the cage-rattling regime.

The abrupt drop in \( P^*(\tau_\ell \geq t) \) for the longest timescales in the short trajectory is due to a bias in the way that the data were sampled. As the trajectory is only a finite length, the full lifetime of the instances of 13A clusters cannot be known. For every instance of a 13A cluster that is identified, it is not known if its starting and ending times \( t_s \) and \( t_e \) are those detected within the trajectory, or in fact lie outside of the window of the trajectory. The effect of this bias is to strictly underestimate the true lifetime of the 13A clusters, and is the cause of the abrupt drop of \( P^*(\tau_\ell \geq t) \) in figure 6.4(b). This sampling issue is addressed in the following analysis of the ‘long’ trajectory.

### 6.3.4. Analysis of the long trajectory

The analysis of the short trajectory demonstrated that the microscopic fluctuations of particles within their cage of neighbours mean that clusters tend to break-up and reform again after a short period. Performing the analysis on IS configurations was not successful in removing this consequence of the microscopic fluctuations, and it was deemed necessary to join together consecutive instances of the same cluster that are separated by periods where the instance is not detected.

We proceed to consider the lifetime autocorrelation function for the longer of the two trajectories, red lines in figure 6.3. The long trajectory totals 300\( \tau_\alpha^A \) in length with configurations separated by 0.1\( \tau_\alpha^A \), which is approximately the total length of the short trajectory.

The long trajectory encompasses many structural relaxation times and the liquid structure is expected to completely relax on this timescale. The ISF \( F_s^A(k_p, t) = 0 \) at long enough times in the trajectory and the particles diffuse throughout the whole simulation box, as shown by the second plateau that develops in \( \langle \delta r^2(t) \rangle \) for large \( t \) in figure 6.3(b). This plateau is an artifact of the fact that particle displacements through the side of the simulation box were not tracked in the calculation of \( \langle \delta r^2(t) \rangle \), thus limiting the maximum displacement to less than the box side length \( L \). When defining the cluster lifetime by the time difference between the first and last configurations that an instance
of a cluster is detected by the TCC algorithm, there is risk that the lifetime will be over-estimated or unphysical if the particles disperse only to form the cluster again later, or that another structure of the particles is predominant during periods where the cluster is not witnessed.

To address this issue a limit is placed for the maximum time that a cluster can break up before later reforming, for its lifetime is taken to continue over this period. The limit is chosen as \( \tau^A \), such that if an instance of the cluster breaks-up and reforms again after more than \( \tau^A \) it is recorded as two separate instances. Conversely, if an instance of a cluster disappears for less than \( \tau^A \), the total lifetime is taken to be continuous across this period.

The limit \( \tau^A \) is chosen as it is of the same order of magnitude of the timescale for dynamical heterogeneities in the liquid, and is around the time expected for any structural order that is related to dynamic heterogeneities. It should be noted that the \( P^*(\tau_{\ell} \geq t) \) obtained will necessarily depend on the choice of this time limit. If the limit is too short then the uncorrected lifetime autocorrelation function \( P(\tau_{\ell} \geq t) \) is recovered (cf. figure 6.4(a)), or if taken to be long there is a risk that spuriously long cluster lifetimes will result, or that one type of cluster is inferred to exist at the same time as another incompatible type of structural order (e.g. 13A and FCC clusters).

We implement a further check on the status of the particles in the periods where a cluster is not detected. It is checked at each frame that no subset of the particles becomes un-bonded from the rest in the cluster. This ensures that all of the particles within the cluster are connected via bonds between the clustered particles, and that the cluster does not physically ‘break-up’ while it is not detected by the TCC algorithm.

The use of a ‘disappearance’ time limit enables the sampling bias seen for the short trajectory to be controlled in the long trajectory. As no cluster may go undetected for \( \tau^A \) during its lifetime, all instances where the initial and final detection points occur between \( \tau^A \) and 299\( \tau^A \) in the long trajectory will necessarily have complete lifetimes.

The clusters that are identified in either the first or final \( \tau^A \) of the trajectory are discarded. The numbers of discarded clusters are small compared to the total that contribute to \( P^*(\tau_{\ell} \geq t) \), hence we are confident that the results are not significantly skewed by discarding clusters in this way.

Figure 6.5(a) shows the lifetime autocorrelation function \( P^*(\tau_{\ell} \geq t) \) as measured from the long trajectory. The initial value of \( P^*(\tau_{\ell} \geq t) \) indicates that 40% of the 13A icosahedra have lifetimes greater than 0.1\( \tau^A \), in agreement with the trend of the short trajectory before the sampling bias becomes significant (figure 6.5(b)). There is a smooth decay of \( P^*(\tau_{\ell} \geq t) \) for longer lifetimes. The graph indicates 15% of the icosahedra have lifetimes greater than \( \tau^A \).

The definition of cluster lifetime used means that icosahedra may be recorded to exist
at certain times when they are not detected by the TCC algorithm. This results in an increase in the fraction of particles participating within icosahedral clusters compared with the fraction detected with the purely static TCC algorithm. It is found that 13.5% of the particles are within icosahedra at this state point, and this increases to 22.7% by inclusion of the particles that are inferred to be within icosahedra.

The lifetime autocorrelation function indicates that only 15% of the icosahedra have lifetimes greater than $\tau^A_{\alpha}$, but this does not imply that only $22.7 \times 0.15 \approx 3.4\%$ of the particles participate in icosahedra with lifetime greater than $\tau^A_{\alpha}$. The reason for this is that each particle can often be found in more than one icosahedral cluster, and the icosahedral clusters will each have individual lifetimes.

In figure 6.5(b) we plot $N_{13A}^*(\tau_\ell \geq t)/N$, which is the number of particles in each configuration participating in icosahedra with lifetime $\tau_\ell \geq t$. If a particle is a member of more than one icosahedral cluster, the longest lifetime cluster is taken when calculating $N_{13A}^*(\tau_\ell \geq t)$. There is a smooth decrease in this function with time. We see that $N_{13A}^*(\tau_\ell \geq \tau^A_{\alpha})/N = 0.131$, i.e. 13.1% of the particles participate in icosahedra with lifetime greater than $\tau^A_{\alpha}$.

In this section we have considered the measurement of cluster lifetimes in supercooled liquids, using 13A icosahedral clusters in the Wahnström supercooled liquid as the test case. We have defined a way by which lifetime autocorrelation functions can be measured for clusters within supercooled liquids, thus characterising the average dynamic behaviour of the cluster. In chapter 7 we analyse the dynamics of clusters within two model supercooled liquids in detail, and discuss how structured regions of certain clusters are related to slow domains in the dynamic heterogeneities.
6.4. Distinguishing the particle sites in clusters

So far in this chapter we have considered the lifetimes of 6A, 6Z and 13A clusters. In the following chapter we consider the lifetimes of both these clusters and a number of other types of cluster in two model supercooled liquids.

As discussed above, there are two methods by which the algorithm could detect the rearrangement of particles within a cluster. The first method ensures that the time resolution of configurations in a trajectory is such that configurations in which the rearrangement process occurs are represented, and that in these configurations the cluster would be seen to break-up by the TCC algorithm (due to changes in the bonding between the particles as they rearrange).

The second method involves distinguishing the individual particle sites in a cluster, and then detecting if the particle indices change at the sites. As discussed this method is difficult for clusters with a high degree of symmetry between the sites. The TCC algorithm does generically differentiate between different classes of particle sites by virtue of how the detection algorithm works. We take credit for the different types of site that are differentiated by the cluster detection routines, and use these to limit the number of rearrangements that are not detectable when measuring cluster lifetimes in supercooled liquids.

In table 6.1 we list the number of different types of particle site that are distinguished by the TCC algorithm. Rearrangements of particles between sites of different type will result in the end of the lifetime of one instance of a cluster and the formation of a new instance.

Here we define the different classes of particle site in each type of TCC cluster and state how they are differentiated between. The language used follows chapter 3 where the detection routines for the different clusters were outlined.

For the 3A cluster the particle sites are not differentiated between, i.e. all particle sites in the cluster are considered identical and the particle indices stored in ascending order in an array. The same is true for 4A clusters. For the 5A cluster the sp3 ring particles and the spindle particles are taken as separate types of site. As stated in section 6.2.1, no sites are differentiated between in 6A clusters, and for the 6Z cluster there are three types of site: the distinct 5A spindles, the common 5A spindles, and the common sp3 ring particles.

For the 7A cluster there are two classes of site: the sp5 ring particles and the spindles. In a 7K cluster the common 5A spindle, the distinct 5A spindles, the common sp3 ring particles, and the distinct sp3 ring particles are differentiated.

For the 8A cluster the symmetry means that it is possible for four different particles to be sp5b/7A spindles. These four particles are distinguished from the other four particles...
Table 6.1: Summary of the number of different types of particle site within each type of cluster that are differentiable by the TCC algorithm. Rearrangements of particles between sites of different type will result in a new instance of the cluster. This is not necessarily the case if rearrangements occur between sites of the same class.

<table>
<thead>
<tr>
<th>Cluster</th>
<th>m</th>
<th>Types of Site</th>
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<tbody>
<tr>
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<td>1</td>
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<tr>
<td>4A</td>
<td>4</td>
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<tr>
<td>5A</td>
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<td>1</td>
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<tr>
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<td>3</td>
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<tr>
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<td>13</td>
<td>5</td>
</tr>
<tr>
<td>FCC</td>
<td>13</td>
<td>2</td>
</tr>
<tr>
<td>HCP</td>
<td>13</td>
<td>3</td>
</tr>
<tr>
<td>9X</td>
<td>9</td>
<td>2</td>
</tr>
</tbody>
</table>

which must be in the sp5 rings. In the 8B cluster the 7A cluster spindles, the additional particle, the sp5 ring particles bonded to the additional particle, and the other sp5 ring particles are the different types of site. For the 8K cluster the 5A cluster spindles, the common sp3 ring particles, and the other sp3 ring particles are differentiated between.

With the 9A cluster a total of 5 different classes of site are distinguished. These are
each of the spindle particles, the sp4 ring particles in the sp4b cluster containing the first spindle particle, and the other sp4 ring particles. In addition a number of conditions help distinguish the particles bonded to the lowest index sp4 ring particle of the sp4b cluster containing the first spindle particle.

For the 9B cluster the sites of the common 7A spindle, the distinct 7A spindles, the common sp5 ring particles and the distinct sp5 ring particles are distinguished. In addition a number of conditions are placed on the bonding of the distinct sp5 ring particles to the common sp5 ring particles and the distinct 7A spindles.

With the 9K cluster the types of site distinguished are the common 6A spindle, the distinct 6A spindles, the common sp4 ring particles, and the distinct sp4 ring particles.

For the 10A cluster the sp4b spindles and the sp4 ring particles are the two classes of particle site. For the 10B cluster the different sites are the common 7A spindle and the other particles. The 10K cluster inherits the four different types of particle site from the 9K cluster and adds another class for the additional particle. For the 10W cluster there are two different types of site: the common sp5b spindle and the other ‘shell’ particles.

For the 11A cluster the three different classes of site are: the common 6A spindle, the distinct 6A spindles and the sp4 ring particles. The 11B cluster inherits the four different types of site from the 9B cluster and adds another type for the additional particles. Conditions are also imposed as to the bonding of the additional particles to the 9B cluster.

With the 11C cluster there are five types of site: the common 7A spindle, the distinct 7A spindles, the common sp5 ring particles, the sp5 ring particles bonded to the common sp5 ring particles, and the other sp5 ring particles. For the 11E cluster there are three types of site: the spindles of the first and second 7A clusters, and the other sp5 ring particles.

For the 11F cluster the types of site are the common sp3 ring particle, the other 6A spindles, the 5A spindles, and the other 5A sp3 ring particles. The 11W cluster inherits the two classes of site from the 10B cluster and adds another for the additional particle.

The 12A cluster inherits the five distinguished classes from the 11C cluster and includes an extra class for the additional particle. In the 12B cluster four types of site are distinguished: the central 7A spindle, the distinct 7A spindle, the other 7A spindles, and the other sp5 ring particles. For the 12D cluster the 7A spindles and the other sp5 ring particles are distinguished between. For the 12E cluster the 5A spindle particles and the sp3 ring particles are distinguished between. For the 12K cluster the three types of site in the 11A cluster are supplemented with distinction for the site of the additional particle.

As described in section 6.3.2 the classes of sites of the 13A icosahedron as the central particle and the shell particles. For the 13B cluster there are three types of site: the common 7A spindle, the other 7A spindles, and the sp5 ring particles. The 13K cluster
inherits the four different types of site in the 11F cluster and the additional particles are also differentiated between.

For the FCC cluster the central and shell particles are distinguished between. For the HCP cluster the types of site are the central particle, the 5A spindles, and the other 5A sp3 ring particles. The types of site distinguished in the 9X cluster are the central and the shell particles.

6.5. Summary and conclusions

In this chapter we have considered how to define the lifetime of clusters detected by the TCC algorithm. The information required to distinguish instances of a local structure are the indices of the particles that participate in the structure, the type of structure (i.e. which the TCC cluster), and the arrangement of the particles within the cluster. These three factors uniquely determine each instance of a local structure. Differentiating all instances of a cluster with different arrangements of the particles is an involved process, however the TCC algorithm provides in the majority of the cases ways to differentiate different classes of particle site within each cluster, allowing some different arrangements to be identified.

For the simulations of isolated colloidal clusters it was sufficient to define the lifetime of a cluster as the time between frames where it is continuously detected by the TCC algorithm. From this definition it was demonstrated that there is in effect a constant rate of decay of the 6A and 6Z clusters, leading to an exponential form for the lifetime autocorrelation function. The decay rate for the two types of clusters was comparable. In order to satisfy the relative proportions of 6Z and 6A states at equilibrium, it was inferred that 6Z to 6Z transitions must be a factor of at least 22 times more frequent than 6Z to 6A transitions.

The measurement of icosahedral lifetimes in a Wahnström supercooled liquid is somewhat different than for the isolated colloidal clusters. The longer-ranged and softer potential of the Wahnström model means that the fluctuations of the particles within its cage of neighbours are much larger than the fluctuations of the colloids in the isolated clusters. The distortion of the bond network due to these fluctuations means that 13A cluster lifetimes were un-physically short if measured as the time that a cluster was continuously detected by the TCC algorithm.

Fluctuations of the bond network on ballistic timescales were found to exist in the IS configurations, meaning that the lifetimes of clusters detected continuously in IS configurations were not significantly greater than for the raw configurations. The effect of the fluctuations was therefore mitigated by extending the cluster lifetimes across periods where the cluster is not detected by the TCC algorithm. A limit of $\tau_A$ was introduced for
the maximum time that instances of a cluster could be joined together across a period where the cluster is not detected. The effect of this procedure is to strictly increase the number of particles participating within each type of structure, and to ensure that the lifetimes of clusters would be comparable to or greater than the beta-relaxation timescale - a timescale over which the local structure in a supercooled liquid is thought to be constant.

The distribution of lifetimes for a type of local structure are characterised by the lifetime autocorrelation function. The lifetime autocorrelation function is the fraction of particles with lifetime $\tau_\ell$ greater than $t$. The number of particles that participate in clusters with lifetime $\tau_\ell$ greater than $t$ decays more slowly than the lifetime autocorrelation function, as clusters can overlap and particles be members of more than one cluster. In this instance the longest lifetime cluster that a particle is participating in is used to define $N^*(\tau_\ell \geq t)$.

In the following chapter we perform an analysis of the lifetimes of different local structures in the Wahnström and Kob-Andersen supercooled liquids using the methods developed in this chapter.
6.6. Bibliography


CHAPTER 7

Structural-Ordering in Supercooled Liquids

7.1. Introduction

The nature of the rapid increase in viscosity as liquids are cooled towards the glass transition is the subject of many theoretical approaches, however there is no consensus on its fundamental mechanism [1–4]. One plausible scenario is that dense packing leads to self-induced memory effects, which causes slow dynamics [5]. However the mode-coupling theory (MCT) transition predicted by this scenario is not observed on cooling towards the glass transition.

The recent discovery of dynamic heterogeneities, i.e. spatial heterogeneities in the relaxation dynamics that emerge on supercooling [6–9], is suggestive of the importance of a growing dynamic length scale in the slowing down approaching the glass transition. In addition to this dynamical phenomenon, the idea of a structural change leading to vitrification has a long history [10]. It has become clear that a range of glass formers exhibit a change in structure upon the emergence of slow dynamics [11], and it is debated as to whether there exists a static lengthscale that underlies the growing lengthscale for the dynamical correlations.

Broadly speaking two types of structure have been identified: spatially extendable crystal-like ordering [12–15], and non-extendable polyhedral ordering [16–23]. For the former it has been stated that critical-like fluctuations of crystalline order are the origin of dynamic heterogeneities in certain classes of supercooled liquid [13].

The latter concerns particles organised into polyhedra that cannot tile Euclidean space due to geometrical constraints [10, 24]. Instead they form ramified structures with a fractal dimension that is less than the dimensionality of the system, i.e., non-extendable ordering. Some metallic glasses have been shown to exhibit this second type of ordering [25, 26]. The exact relationship of the polyhedral order to the dynamic heterogeneities is unclear, however measurements have shown that the polyhedral domains are slow to
One of the main difficulties of identifying structural correlations in supercooled liquids is that it is not known *a priori* which type of static order is important. Frequently studies have employed structure detection methods, such as Voronoi face analysis (VFA), common neighbour analysis (CNA) or bond orientational order (BOO) analysis, that search for predefined types of structural ‘motif’ and see how the numbers change as a function of temperature [16, 18, 27]. Recently a number of “order-agnostic” schemes have been devised to identify structural correlations without first having to define what structures will be searched for [28–34].

To strengthen the link between structure and glassy behaviour three types of evidence have been presented. Firstly multi-body structural correlation functions have been presented that clearly show structural changes occur on supercooling towards the glass transition [11, 22]. Secondly dynamically slow regions have been correlated with different types of local ordering [11, 20]. Thirdly the presence of structural and dynamic length scales that grow similarly has been sought [12–15].

The case of growing structural and dynamic length scales is controversial. Some authors have identified a direct correspondence between the growing dynamical and structural length scales in polydisperse systems displaying crystal-like ordering [13–15], while others have not [35, 36].

In the case of the Kob-Andersen (KA) binary system known to display polyhedral ordering [11], only weakly growing structural lengthscales have been identified by the order-agnostic “point-to-set” analysis [33], while other approaches using static perturbation of inherent structures [29] and finite size scaling [37] find a much stronger increases in static lengthscales.

Local structural ordering has yet to be found in certain binary hard and soft sphere mixtures. For these systems no one-to-one correspondence between an order-agnostic structural lengthscale and the dynamical lengthscale has been found [31, 34, 35, 38], but static perturbation analysis has suggested a growing structural lengthscale [39].

An interesting case that we examine is the behaviour of static and dynamic lengthscales in the Wahnström mixture [40]. The Wahnström mixture is a binary Lennard-Jones (LJ) system composed of large (A) and small (B) particles. It is a commonly used model for supercooled liquids, however the model can crystallise upon formation of a structure that contains icosahedra composed of six A and six B species around a central B-type particle and Frank-Kasper bonds [22].

Icosahedral order that develops upon cooling has been linked to slow dynamics in this system [11]. It has been suggested that critical-like fluctuations of crystalline-order might underlie the dynamic heterogeneities in this binary system [15], as seen in certain polydisperse quasi-hard sphere systems [13, 15]. In this chapter we find only a weak...
link between crystalline-order and dynamic heterogeneities, and that non-extendable networks of icosahedra incompatible with the crystal structure are formed in the supercooled liquid.

We also consider the KA binary LJ mixture [41]. For this mixture the 11A polyhedral structure has been linked to slow dynamics [11]. This structure frustrates crystallisation, which occurs by phase separation in this system [42]. In this chapter we study the static correlations between the domains of 11A polyhedra in the supercooled liquid.

In this chapter the structure in Wahnström and KA supercooled liquids using the topological cluster classification (TCC) algorithm. We use the algorithm to identify any structural changes that occur in these mixtures on cooling towards the glass transition. We then study the lifetimes of the clusters that are found at deeply supercooled state points in order to gauge which structures are likely candidates to be associated with slow domains of dynamic heterogeneities. Finally we analyse how correlation lengths for the domains of structured particles are related to the growing dynamic lengthscale.

### 7.2. Model and simulation details

We consider the Wahnström and KA mixtures [40, 41]. Details of the interactions between the large (A) and small (B) species were given in chapter 2. The interactions are truncated and smoothed using the Stoddard-Ford method [43]. For the Wahnström model the truncation lengths are \( r_{AA}^{tr} = r_{AB}^{tr} = r_{BB}^{tr} = 2.5 \) [40], and for the KA model the truncation lengths are in proportion to the interaction lengths [41], i.e. \( r_{AA}^{tr} = 2.5, r_{AB}^{tr} = 2.0 \) and \( r_{BB}^{tr} = 2.2 \).

The simulations consist of \( N = 10976 \) particles in 3D with periodic boundary conditions. For the Wahnström model \( N_A = N_B \) and the density \( \rho = 1.296 \), while for the KA model \( N_A = 8781 \) and \( \rho = 1.2 \). Lengths, temperatures and times are quoted in units of \( \sigma_{AA}, \epsilon_{AA}/k_B \) and \( (m_A\sigma_{AA}^2/\epsilon_{AA})^{1/2} \) respectively. The simulations are molecular dynamics (MD) with timestep \( \Delta t = 0.001 \).

The simulations are prepared from a \( T = 5.0 \) state point with the particles initialised at the sites of a face-centred cubic (FCC) crystal. The crystal is melted and equilibrated as a fluid for 100\( \tau_{\alpha}^{A} \) in the \( NVT \)-ensemble using the Nosé-Poincaré (NP) thermostat with coupling parameter \( N_{NP} = 1.0 \). The thermostat was switched off then further equilibration was performed in the \( NVE \)-ensemble using the velocity Verlet algorithm for 1000\( \tau_{\alpha}^{A} \). On completion of the equilibration process, a trajectories of length 300\( \tau_{\alpha}^{A} \) were sampled for analysis.

Trajectories for the lower temperature state points for \( T < 5.0 \) were obtained via a step-wise cooling process. Each new state point was obtained by quenching instantaneously to a lower temperature from an equilibrated configuration of the previous higher
temperature state point. An equilibration process identical to that used for the $T = 5.0$ state point was performed following the quench.

The $\alpha$-relaxation time $\tau_A^{\alpha}$ for each state point is defined by fitting the Kohlrausch-Williams-Watts (KWW) stretched exponential to the alpha-regime of the self self-intermediate scattering function (ISF) of the $A$-type particles. The stability of the deep quenches was checked by ensuring there was no time evolution in the ISF, the partial radial distribution functions $g_{AA}(r)$, $g_{AB}(r)$ and $g_{BB}(r)$, or the number of clusters detected by the TCC algorithm across the trajectories. Crystallisation was not seen in any of the simulations.

### 7.3. Viscous dynamics

In figure 7.1 the viscous behaviour of the supercooled liquids is shown. The ISF is shown for a number of state points in figure 7.1(a) and the relaxation time as a function of inverse temperature is plotted in figure 7.1(b). For the equilibrium liquid state points at high temperatures, the relaxation times are well fitted by an Arrhenius function. As the temperature is lowered a cross-over in the dynamical behaviour occurs and the relaxation times increase faster than predicted by the Arrhenius equation. This ‘super-Arrhenius’ increase in relaxation times on supercooling is one of the most distinctive features of glassy behaviour.

We fit the two regimes for the relaxation time delimited by an onset temperature for slow dynamics $T^*$ [11]. For $T > T^*$ an Arrhenius form is used, while for lower temperatures the Vogel-Fulcher-Tammann (VFT) equation is fitted [44–46]. A number of theories that associate the glass transition with an underlying thermodynamic phase transition, such as the Adam and Gibbs, random first order transition (RFOT), and two-order parameter theories [1, 47], predict that $\tau_A^{\alpha}$ should follow a VFT form in the supercooled
regime, and that there is a finite temperature glass transition $T_0$ where the dynamical relaxation time diverges.

The fitting for $\tau^A_\alpha$ is

$$
\tau^A_\alpha = \begin{cases} 
\tau_\infty \exp\left[\frac{E_\infty}{k_B T}\right] & \text{for } T \geq T^*, \\
\tau'_\infty \exp\left[\frac{D}{T-T_0}\right] & \text{for } T < T^*. 
\end{cases}
$$  \hspace{1cm} (7.1)

The quantities $\tau_\infty$ and $E_\infty$ are fitting parameters for the Arrhenius equation, while $D$ is the fragility of the glass-former (the higher the fragility the lower the value of $D$) and $T_0$ is the temperature at which the relaxation time diverges in the VFT equation. The constant $\tau'_\infty$ is fixed such that equation 7.1 is continuous. The values of the fitting parameters are shown in table 7.1 and the fits in figure 7.1(b).

### 7.4. Structural analysis

#### 7.4.1. Fraction of particles participating within clusters

We analyse how the particles in the supercooled liquids are structured using the TCC algorithm. The bonds are detected from the particle coordinates using the modified Voronoi method with a maximum bond length cut-off of $r_c = 2.0$ for all types of interaction (AA, AB and BB). For the Wahnström mixture $f_c = 0.82$, however for the KA mixture we choose $f_c = 1.0$. The latter value is chosen as the 11A cluster that is suggested to be important for the slow dynamics in the KA mixture [11] has a wide distribution of bond lengths in the cluster\(^1\), therefore detection of the cluster is better when using higher values of $f_c$ to incorporate longer bonds into the bond network.

In figure 7.2 we plot the fraction of particles detected within each type of cluster, $N_C/N$, for the Wahnström mixture. The onset temperature for slow dynamics is indicated by the orange dotted line on each of the plots. It is clear from these order parameters that the liquid sees continuous changes in local structure as it is cooled.

\(^1\)See discussion in section 3.7.11 of chapter 3.

<table>
<thead>
<tr>
<th></th>
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<th>KA</th>
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<tr>
<td>$T^*$</td>
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<td>1.00</td>
</tr>
<tr>
<td>$T_0$</td>
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<td>0.250</td>
</tr>
<tr>
<td>$D$</td>
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<td>7.48</td>
</tr>
<tr>
<td>$\tau_\infty$</td>
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</tr>
<tr>
<td>$E_\infty$</td>
<td>2.04</td>
<td>2.91</td>
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</table>

Table 7.1: Fitting parameters for the relaxation data with the hybrid Arrhenius-VFT fit.
Figure 7.2: The fraction of particles participating in each cluster type for the Wahnström mixture. The dotted orange lines mark the onset temperature of slow dynamics $T^*$. (a) Clusters 5A to 8K, (b) 9A to 11A, (c) 11B to 12D, (d) 12E to 13K and the crystal clusters.
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The majority of clusters see an increase in their numbers upon cooling. Other clusters show a non-monotonic behaviour (e.g. 9K, 9X). All of the particles are identified within certain simple structures such as the 5A triangular bipyramid irrespective of temperature, while other more complicated clusters, such as 10K, 11B and HCP, are almost never seen.

The behaviour of the icosahedral clusters is hierarchical. The number of particles within 13A icosahedra increase from 0 to 20% over the temperature range studied, while the number of particles within sub-clusters of the 13A icosahedra such, as 10B, 11C and 12B, also increase on cooling. It is strictly necessary that the number of particles within the sub-clusters is greater than the number within 13A clusters.

Given the variety and range of structural changes that occur, it is not clear a priori which of the structures, if any, are important for the formation of dynamic heterogeneities on cooling. It should not be assumed that just because structural changes occur within the supercooled regime that they are responsible for the formation of dynamic heterogeneities, as structural changes also occur in the Arrhenius regime which is not characterised by glassy behaviour.

The local structures detected the KA mixture as a function of inverse temperature are plotted in figure 7.3. As for the Wahnström mixture there are a range of different structural changes that occur on cooling. The numbers of particles within 11A, 11W, 12B, 12E and 12K clusters show the largest relative increases in the super-Arrhenius regime. Moreover, the rate of increase in these clusters grows upon further supercooling.

As for the Wahnström mixture we find structural changes that occur in the Arrhenius regime, as well as the super-Arrhenius regime. We also find clusters in which almost all particles participate in, while other clusters are only seen in trace quantities. The number of particles in 9A and 9X clusters decreases on cooling.

The question remains as to how to determine the contribution of the different structures to the glassy behaviour and dynamical heterogeneities of the supercooled liquid.

7.4.2. Cluster lifetime distributions

We employ the algorithm developed in chapter 6 to measure the lifetimes of the different TCC clusters at the lowest temperature state points for each of the supercooled liquid models. The ‘instances’ of each cluster are defined by the indices of the particles within the cluster, the type of TCC structure, and in-part the arrangement of the particles within the cluster to a certain. Each instance cluster occurs between two frames in the trajectory and the lifetime is the difference in time between these frames. Any periods where the instance is not detected by the TCC algorithm are shorter than $\tau^A_\alpha$ in length and no subset of the particles becomes un-bonded from the others in the cluster during these periods.

The measurement of lifetimes for all the instances of clusters in these $N = 10976$ sim-
Figure 7.3: The fraction of particles participating in each cluster type for the KA mixture. The dotted orange lines mark the onset temperature of slow dynamics $T^*$. (a) Clusters 5A to 8K, (b) 9A to 11A, (c) 11B to 12D, (d) 12E to 13K and the crystal clusters.


Figure 7.4: Lifetime autocorrelation functions for the clusters in supercooled liquids. \( P^*(\tau \geq t) \) for (a) the Wahnström liquid at \( T = 0.604 \) and (b) the KA liquid at \( T = 0.498 \).

Simulations is intensive in terms of the quantity of memory required to store the instances and the number of searches through the memory required by the algorithm each time an instance is found. We do not measure lifetimes for the clusters where \( N_C/N > 0.8 \) for the \( T = 0.604 \) Wahnström or \( T = 0.498 \) KA state points under consideration. These clusters are pervasive across the system hence it is difficult to argue that these structures are related to spatial heterogeneities in the dynamics. It is conceivable for the number of these clusters \( \mathcal{N} \) to be heterogeneous across the system and hence there opening up a possible relationship to dynamic heterogeneities at this level of detail, however in practice we find that the spatial density of clusters with \( N_C/N > 0.8 \) is reasonably homogeneous.

In figure 7.4 we plot the lifetime autocorrelation function \( P^*(\tau \geq t) \) for the lowest temperature Wahnström and KA state points. Figure 7.4(a) clearly shows that the most persistent or the longest lived of the different types of clusters are the 13A icosahedra. All other clusters display lifetime autocorrelation functions that decay more quickly than for 13A. Icosahedra are found in the crystal structure of this mixture suggesting a possible link between crystalline order and glassy behaviour. The long-time tail of the icosahedral autocorrelation function indicates that some of these clusters preserve their local structure on timescales far longer than \( \tau_{\alpha}^A \). As we shall see below, this effect is enhanced when the icosahedra group into domains.

There is a slowly decaying component of the 8K cluster lifetime distribution function that approaches \( P^*(\tau \geq t) \) for icosahedra for long times. It is found that the arrangement of the particles in the 8K clusters with long lifetimes are identical to that of ‘Frank-Kasper’ clusters. Frank-Kasper clusters are a particular type of 8K cluster with six \( B \)-species are common neighbours of a pair of \( A \)-species particles. Frank-Kasper clusters form part of the crystalline structure of this model [22].

A number of clusters related to the 13A icosahedra have been excluded from figure
7.4(a) for clarity. The clusters excluded are 9B, 10B 11C and 12B, which are sub-clusters of 13A, and 11E and 12D, which occur at ‘α-’ and ‘β-sites’ where two icosahedra share a face or a five-membered ring of particles [18, 48]. The lifetime autocorrelation function for these clusters is bounded by that for 13A, solid purple line in figure 7.4(a).

The lifetimes of all cluster types hold no simple relationship to their size and frequency of occurrence. For example the four-fold symmetric \( n = 6 \) particle 6A octahedral cluster is smaller and 8 times more numerous than icosahedral clusters, yet displays far quicker decay of \( P^*(\tau^_t \geq t) \). There is no trend in the rate of decay of the lifetime correlation function for the ground-state clusters relative to other clusters of equal size. For example the ground state 8A cluster has an average lifetime that is lower than the 8K cluster, and likewise the ground state 11W cluster has shorter lifetimes than 11B or 11F clusters on average. This result goes against the Frank conjecture that it would be the ground state clusters that are most stable [10]. Moreover there is no monotonic trend in the lifetime of the ground state clusters with the cluster size, as the 6A, 8A and 11W have correlation functions \( P^*(\tau^_t \geq t) \) that decay more quickly than the 5A, 7A, 8B, 9B, 10B, 12B and 13A ground state clusters\(^2\).

The fast initial drops of \( P^*(\tau^_t \geq t) \) reflect the existence of large numbers of clusters with lifetimes \( \tau^_t \ll \tau^A_α \). The lifetime of these clusters is comparable to the timescale for beta-relaxation where the particles fluctuate within their cage of neighbours. It could be argued that these clusters arise spuriously due to the microscopic beta-fluctuations, and that the short-lived clusters are not representative of the actual liquid structure. However the weakness in this argument for the icosahedra is that almost no 13A clusters are found at higher temperatures, cf. figure 7.2, where microscopic fluctuations in the beta-regime also occur. We have also not found a way to distinguish between the short and long-lived icosahedra structurally. Therefore it must be accepted that the measured distribution of icosahedral lifetimes, which includes short-lived icosahedra, is representative of the true lifetime distribution for icosahedra. We will see below that as icosahedra overlap, one particle may be a member of multiple icosahedra and that the majority of particles found in short-lived icosahedra are also participating in longer-lived icosahedra. In other words short- and long-lived icosahedra mainly lie in the same regions of the liquid.

Another interpretation for the initial drop in \( P^*(\tau^_t > t) \) of the clusters is that our intuition that there is constant local structure in the beta-regime, which then relaxes on the timescale of the alpha-regime is incorrect. It may be the case that microscopic ballistic and cage-rattling motions are enough to reorder local structures without relying on the ‘cage-hopping’ motions of the alpha-regime. It has been seen in previous studies that glasses can crystallise on a timescale before the diffusive range of the mean-square

\(^2\)This result was obtained in \( N = 1000 \) simulations where sufficient computational resources were available to measure the lifetime autocorrelation function for the 5A, 7A and 9B clusters.
displacement (MSD) is reached, and occurs with most particles moving by less than one diameter [49, 50]. These results demonstrate that in practice local structure can relax into a distinct structure by only small movements of the particles, and if this mechanism is at play in the supercooled liquids it would explain the initial drops of $P'(\tau \geq t)$ that occur on the timescale of $\approx 0.1 \tau^A\alpha$.

Moving on to the KA mixture, we show the cluster lifetime autocorrelation functions in figure 7.4(b). As for the Wahnström mixture there is a single cluster, the 11A polyhedron, demonstrating slow decay of the lifetime autocorrelation function relative to all the other clusters. The clusters with lifetime autocorrelation functions most similar in magnitude to the 11A cluster are 11W and 12K. The 12K cluster is an 11A cluster with an additional particle bonded to it, and there is a high degree of overlap between the 11W clusters and the 11A clusters as their bonding is similar, hence we conclude that both of these clusters are related structurally to the 11A clusters. The lifetime autocorrelation function there indicates which of the local structures identified by the TCC algorithm are most stable in the KA mixture. The long-lived clusters are candidates by which structured particles and slow domains of dynamic heterogeneities may be linked.

Comparing the results for the Wahnström mixture with the KA mixture, we note that the decay of the lifetime autocorrelation function for icosahedra is slower than for the 11A polyhedra, indicating that there are structured domains in the Wahnström mixture that are longer lived than the KA mixture when comparing these two state points. It has been suggested that the difference in the numbers and stability of local structures explains the difference in fragility of the models [11]. We exercise caution on drawing conclusions on this question with our data as the relaxation times and the degree of super-Arrhenius behaviour are different between the $T = 0.604$ Wahnström and $T = 0.498$ KA state points that we have studied.

Like for the Wahnström mixture, we also note that the values of $P'(\tau \geq 0.1 \tau^A\alpha) < 0.3$ for all types of clusters, indicating that the majority of clusters have short lifetimes relative to the alpha relaxation time.

7.4.3. Composition and dynamics of particles in long-lived clusters

The structural analysis above was performed by treating all particles identically with the TCC algorithm. Here we examine the composition of the 13A icosahedra and 11A polyhedra in terms of A- and B-species. For both clusters we find that the central particle is a B-particle in $> 99\%$ of all instances.

In figure 7.5 we plot the compositions of the shell particles of each cluster. From figure 7.5(a) it is clear that there is a distribution of compositions of $A-$ and $B-$ species in the shell of 13A icosahedra. There are two arrangements of $m_A = 6 A$-particles in the shell
Chapter 7. Structural-Ordering in Supercooled Liquids

Figure 7.5: Composition of the (a) 13A clusters in the Wahnström mixture and (b) 11A clusters in the KA mixture. On average each cluster has a small B-species as its central particle, $m_A$ is the number of A-species in the shell of the cluster. The height of the bars show the relative proportions that each of the compositions occurs.

that are compatible with the crystal structure [22]. There are only 30% of the 13A with $m_A = 6$ however, and moreover arrangement of the particles in the shell compatible with the crystal is still not guaranteed. This result indicates that the majority of icosahedra found in the supercooled liquid have defective crystalline order because the arrangement of the particles is rarely as occurs within the bulk crystal.

For the KA mixture the majority of 11A clusters have $m_A = 10$ A-species in the shell of the cluster (figure 7.5(b)). We note that this arrangement maximises the number of AB bonds for the central B-particle, which is energetically favourable for the central B-particle with the KA LJ interactions.

In figure 7.6 we examine how the dynamics of the 13A icosahedra translates into the dynamics of individual particles. Figure 7.6(a) shows the number of particles within icosahedral clusters as a function of the cluster lifetime. Although there is a fast initial drop in the lifetime autocorrelation function of 13A clusters on the beta-relaxation timescale (figure 7.4(a), solid purple line), as the icosahedra overlap there remains a significant fraction of the particles participating in the 13A clusters with lifetimes comparable to the dynamic heterogeneities $\approx \tau^*_A$. The difference between $N^*_{13A}(\tau_\ell \geq 0.1 \tau^*_A)/N$ and $N^*_{13A}(\tau_\ell \geq 0)/N$ indicates that only 3% of the particles are members of icosahedra with $\tau_\ell < 0.1 \tau^*_A$ and not a member of an icosahedron with a longer lifetime as well.

Figure 7.6(b) shows the MSD of the particles identified initially within icosahedral clusters (coloured lines) and compares this to the system-wide MSD (black line). All of the particles within icosahedra relax more slowly than the average (red line), and the time they take to attain diffusive motion increases as the lifetime of the icosahedra in which they participate in increases. In other words the longer the lifetime of the icosahedra,
the slower the particles within them become. Since some icosahedra last for very long times (figure 7.4(a)), it is expected that these particles may exhibit very low mobilities as they maintain some of their nearest neighbours throughout (e.g. the central particle will always have the shell particles as its nearest neighbours). For the longest lived icosahedra (blue lines) there is a delay for the MSD to leave the plateau compared to the shorter lived icosahedra, i.e the effect is to shift the curves along the $t$-axis. This shift, indicating that the particles in the long-lived icosahedra are initially slower on average, goes away at longer times as the graph is plotted with logarithmic scales, and as such the resolution needed to see the shift is lost.

A similar analysis is performed for the KA mixture in figure 7.7. There are significant numbers of particles within 11A clusters with lifetimes comparable to that for the dynamic heterogeneities (figure 7.7(a)). Figure 7.7(b) shows that particles within 11A clusters relax more slowly on average, and that the longer-lived the clusters the slower the relaxation of the particles that are involved. The effect of 11A clusters on the particle dynamics is smaller than what is observed with 13A clusters in the Wahnström mixture, as there are fewer particles in clusters of lifetime $\tau_{11A} \geq 3 \tau_{11A}^A$.

### 7.4.4. Analysis of the structured domains

On cooling the number of icosahedra in the Wahnström mixture and 11A clusters in the KA mixture increase. At high temperatures the clusters are generally isolated from each other. As the temperature is lowered and the number of clusters increases, domains of clustered particles form. In this section we analyse the character of these domains of clustered particles and determine the effect the domains have on individual particle dynamics.
The domains of icosahedra that form on cooling in the Wahnström mixture are shown in figures 7.8(a)-(c). At high temperature icosahedra are predominantly isolated (figure 7.8(a)). Upon cooling, the icosahedra overlap and join together (figure 7.8(b)) to form (transient) networks at low temperatures (figure 7.8(c)).

In order to investigate the structure of the domains, we calculate their radius of gyration,

\[ R_G = \frac{1}{2n^2} \sum_{i,j} (\mathbf{r}_i - \mathbf{r}_j)^2, \]

where \( n \) is the number of particles in the domain and the double sum extends over all pairs of particles in the domain. For configurations where the domains of icosahedra percolate throughout the simulation box \( R_G \) cannot be defined. These configurations are rare at \( T = 0.620 \) and are excluded from the analysis. The consequences of percolating icosahedral domains are discussed further below.

The radius of gyration shows a power law growth in the size of the domain \( n \) with an exponent of 0.47 and amplitude of 0.32 (figure 7.8(d)). In other words the domains have a fractal dimension \( d_f \approx 2 \), indicating that they are not space-filling.

The individual icosahedra have enhanced stability as the size of the icosahedral domains grow (figure 7.8(e)). The time \( \tau_\ell \) is the mean lifetime of icosahedral clusters within a domain of size \( n \) in a configuration. For \( T = 0.620 \), this grows almost five-fold as the domain size increases from isolated icosahedra (\( n = 13 \)) to extended domains of icosahedra (\( n \approx 200 \)).

For higher values of \( n \), it appears that \( \tau_\ell \) may saturate. Our data are limited by system size for these large icosahedral domains, so the result needs to be treated with caution. If indeed there is indeed saturation in \( \tau_\ell \) with \( n \), this would suggest that there is a maximum...
Figure 7.8: Analysis of the domains of 13A particles in the Wahnström mixture. (a)-(c) Domains of icosahedral clusters form on cooling from high to low temperature (slices through 3D simulation box). Particles in icosahedral clusters are shown full size in green, other particles are blue dots. (d) The radius of gyration $R_G$ of the domains versus the number of particles in the domain $n$ for $T = 0.620$. $R_G$ is well fitted by $0.32n^{0.47}$ indicating the domains have a fractal dimension $d_f \approx 2$. (e) The mean lifetime of icosahedral clusters $\bar{\tau}_\ell$ versus the domain size $n$. (f) Icosahedral domains retard the motion of neighbouring particles. The MSD $\langle \delta r^2(\tau_h) \rangle$ as a function of distance from icosahedral domains $d$ (solid line). The dotted line is the MSD over $\tau_h$ of all particles not in icosahedra, independent of $d$. Note that the particles located around $d = 1$ amount to 40% of the system at this temperature.
stability for 13A clusters, likely to occur when a 13A cluster is maximally surrounded by other 13A clusters. If this is the case, upon percolation where \( n \) diverges, \( \bar{\tau}_e \) would see no further increase and full dynamical arrest would not be expected, as indeed we find at the lower temperature \( T = 0.604 \) state point.

We now consider the effect the domains have on the remainder of the system. In figure 7.8(f), we plot the MSD of the non-icosahedral particles \( \langle \delta r^2(t_h) \rangle \) against the distance \( d \) from the nearest icosahedral particle at time \( t = 0 \). The time \( \tau_h \approx \tau_{A,\alpha} \) is the time of the maximum in the dynamic susceptibility \( \chi_4(t) \) defined below [2]. The first nearest neighbours of the domains have suppressed mobility, indicating coupling between the structured domains and the dynamics of the neighbouring particles. Correspondingly the second and third shells of neighbours of the domains have higher mobility compared to the average for non-icosahedral particles, indicating there is a hierarchy of spatial dynamics related to domains of icosahedra.

In figure 7.9 the domains of 11A polyhedra in the KA model are analysed. Again, the results for the two models are broadly similar. On cooling domains of 11A clusters develop, figures 7.9(a)-(c). Analysis of the radius of gyration of the domains indicates that the fractal dimension of the domains is \( d_f \approx 2 \), figure 7.9(d). Percolating domains are seen much less frequently for the KA \( T = 0.498 \) state than for the Wahnström \( T = 0.620 \) state point, as the number of clustered particles are fewer \( N_{11A}(\tau_e \geq 0)/N = 0.24 \) versus \( N_{13A}(\tau_e \geq 0)/N = 0.26 \).

The lifetimes of the 11A clusters are shorter than for the 13A icosahedra, as indicated by the faster decay of \( P^*(\tau_e \geq t) \) (figure 7.4). Figure 7.9(e) shows that the lifetime of the 11A clusters increases more moderately than the 13A clusters with the size of the domain. The peak at \( n = 16 \) indicates there is a particularly stable arrangement of two 11A clusters involving sixteen particles, relative to other domains of a similar size. No saturation in \( \bar{\tau}_e \) is seen with increasing domain size.

Figure 7.9(f) shows the effect of the 11A domains on the dynamics of other particles in the liquid. For distances \( d < 0.96 \) the particles selected are mainly B-species due to the nature of the KA LJ interactions. These particles are more mobile than the majority A-species, independent of \( d \), due to their smaller size. The number of particles with \( d < 0.96 \) of a 11A domain is around 10% of the system, i.e. half of the B-species.

Moving further away from the 11A domains, there is then a region of particles with \( d \approx 1 \) with reduced mobility compared to the average for non-11A particles (dotted line in figure 7.9(f)). Around 37% of the particles are found in this region. Subsequent neighbours of the 11A domains for \( d > 1.26 \) have increased mobility relative to the average. As with the 13A domains in the Wahnström mixture, the results show that the presence of the 11A domains with stable structure alters the dynamics of the surrounding liquid, indicating that the dynamics are spatially correlated with domains of 11A clusters.
Figure 7.9: Analysis of the domains of 11A particles in the KA mixture. (a)-(c) Domains of 11A clusters form on cooling from high to low temperature (slices through 3D simulation box). Particles in 11A clusters are shown full size in red, other particles are blue dots. (d) The radius of gyration $R_G$ of the domains versus the number of particles in the domain $n$ for $T = 0.498$. $R_G$ is well fitted by $0.32n^{0.48}$ indicating the domains have a fractal dimension $d_f \approx 2$. (e) The mean lifetime of 11A clusters $\bar{\tau}_\ell$ versus the domain size $n$. (f) 11A domains affect the motion of neighbouring particles. The MSD $\langle \delta r^2(\tau_h) \rangle$ as a function of distance from 11A domains $d$ (solid line). The dotted line is the MSD over $\tau_h$ of all particles not in 11A clusters and independent of $d$. 
7.5. Analysis of correlation lengths

Finally we consider whether the structured domains of particles in the Wahnström and KA mixtures are related to the increasing dynamic correlation length in the supercooled liquids.

7.5.1. Dynamic correlation length

We follow Lačević et al. in our calculation of the dynamic correlation length \( \xi_4 \) [51]. A particle site overlap function is defined as

\[
w(|r_j(0) - r_l(t)|) = \begin{cases} 
1 & \text{for } |r_j(0) - r_l(t)| \leq h, \\
0 & \text{otherwise}, 
\end{cases}
\]

where \( h \) is a length parameter defining the size of the particle site. The function selects the particle sites at time 0 that are occupied at time \( t \). The fraction of overlapping particle sites between two configurations is

\[
Q(t) = \frac{1}{N} \sum_{j=1}^{N} \sum_{l=1}^{N} w(|r_j(0) - r_l(t)|). 
\]

The fluctuations of this time dependent order parameter is the dynamic susceptibility \( \chi_4(t) \):

\[
\chi_4(t) = \frac{V}{N^2 k_B T} [\langle Q(t)^2 \rangle - \langle Q(t) \rangle^2]. 
\]

The dynamic susceptibility is a time-dependent function that has a peak at \( \tau_h \simeq \tau_A^4 \). The amplitude of the peak indicates the number of particles that are involved in regions of correlated motion. In other words \( \chi_4(t) \) indicates the existence of dynamical heterogeneities and the extent to which the motions of particles are correlated in space\(^3\). We fix the diameter of the particle sites as \( h = 0.3 \), which maximises the amplitude of the peak in \( \chi_4(t) \) for the Wahnström mixture [51].

The dynamic susceptibility for the Wahnström mixture is shown in figure 7.10(a). The data are calculated as the average of \( \chi_4(t) \) over six trajectories of length \( 300 \tau_A^4 \).

The dynamic susceptibility informs us of the timescale for which the spatial correlations between regions of immobile particles are maximised. We extract a lengthscale from the correlations with the four-point dynamic structure factor \( S_4(k, t) \):

\[
S_4(k, t) = \frac{1}{N^2 \rho} \sum_{jl} \exp[-i k \cdot r_j(0)] w(|r_j(0) - r_l(t)|) \sum_{mn} \exp[i k \cdot r_m(0)] w(|r_m(0) - r_n(t)|). 
\]

\(^3\)The choice of \( h \) means that correlated particles are in fact better described as immobile rather than in motion.
Figure 7.10: (a) The dynamic susceptibility $\chi_4(t)$ of the Wahnström mixture. The maximum of $\chi_4(t)$ occurs at time $\tau_h$. (b) The four-point dynamic structure factor $S_4(k, \tau_h)$. (c) The structure factor of the icosahedral particles $S_{13A}(k)$. Here $N_{13A} = N_{13A}(\tau \ell \geq 0)$. In (b) and (c) the solid lines are fits to the data with the Ornstein-Zernike expression.

We assume that the spatial heterogeneities in the dynamics are isotropic and consider the angularly averaged version of the four-point structure factor $S_4(k, \tau_h)$ over $\tau_h$. The four-point structure factor is shown in figure 7.10(b) for the Wahnström supercooled state points.

The low-$k$ behaviour of $S_4(k, \tau_h)$ is found to be well-fitted by an Ornstein-Zernike expression

$$S_4(k, \tau_h) = \frac{S_4(0, \tau_h)}{1 + [k \xi_4(\tau_h)]^2}$$

suggesting a link between dynamic heterogeneities and critical-like behaviour [52]. The correlation length that is extracted is $\xi_4$.

The fits of $S_4(k, \tau_h)$ for $k < 2$ are shown in figure 7.10(b). The size of the correlation length extracted via this procedure has been shown to have a small dependency on the size of the simulations [53]. The results we obtain for our $N = 10976$ particle simulations are consistent with previously published results for the two mixtures [51, 53, 54].

### 7.5.2. Static correlation lengths

We consider two static correlation lengths for the domains of structured particles in the Wahnström and KA mixture. The first method allows for direct comparison with the dynamic lengthscale. We define a structure factor restricted to the particles identified within clusters:

$$S_C(k) = \frac{1}{N\rho} \left( \sum_{j=1}^{N_C} \sum_{l=1}^{N_C} \exp[-i\mathbf{k} \cdot \mathbf{r}_j(0)] \exp[i\mathbf{k} \cdot \mathbf{r}_l(0)] \right),$$

where $N_C$ is the number of clustered particles. We then fit the Ornstein-Zernike equation to the low-$k$ behaviour of $S_C(k)$ in order to extract a structural correlation length $\xi_{SC}$. 
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Figure 7.11: (a) The relationship between icosahedra and spatial heterogeneities in the dynamics for the Wahnström mixture at $T = 0.604$ (2D slice of simulation box). Mobility $\langle \delta r^2(\tau_h) \rangle$ is depicted by the size of the particle. Large particles have $\langle \delta r^2(\tau_h) \rangle < 0.043$, small particles otherwise. Particles always within icosahedral clusters with lifetime $\tau_\ell \geq \tau_4^A$ are coloured green, and others are grey. Structural $\xi_{RG}$ (squares) and $\xi_{SC}$ (crosses), and dynamical $\xi_4$ (circles) correlation lengths for the (b) Wahnström and (c) Kob-Andersen mixtures.

This procedure is akin to the calculation of the dynamic lengthscale $\xi_4$: first a structure factor is calculated from a selected fraction of the particles (either immobile or structured) in each configuration, and the Ornstein-Zernike expression used to extract a correlation length. The structure factor for the 13A particles in the Wahnström mixture with the Ornstein-Zernike fits is shown in figure 7.10(c).

The second lengthscale we consider for the structured particles is derived from the radius of gyration of the domains of clusters. We define

$$\xi_{RG} = R_C^2\langle n \rangle/m^{1/d_\ell}, \quad (7.9)$$

where $R_C^2$ is the radius of gyration of a single cluster, $\langle n \rangle$ is the ensemble average of the domain size, $m$ is the number of particles in the cluster, and $1/d_\ell$ is the exponent of the power law fitted to $R_G$ versus $m$. This correlation length does not probe the correlations between the domains, as per $\xi_{SC}$, rather it characterises the growth in size of the domains on cooling until a percolation transition is reached.

7.5.3. Comparison of the correlation lengths

The temperature behaviour of the different correlation lengths are shown in figures 7.11(b) and (c) for the Wahnström and Kob-Andersen mixtures respectively. All three correlation lengths increase on cooling, however the manner in which each of the lengths increases
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is quite different.

The main result for both mixtures is that the growth in the dynamic correlation length $\xi_4$ is not matched by the growth in the structural correlation length $\xi_{SC}$. We have measured structural correlation lengths in a number of ways: by considering structured particles as detected directly from the configurations by the TCC algorithm; with the inclusion of additional structured particles due to the dynamic analysis (chapter 6); with the inclusion of neighbouring particles with reduced mobility; or lengths from domains of related clusters of 13A (12D, 8K, Frank-Kasper) or 11A (11W and 12K). However the growth of the structural correlation lengthscales in all these cases is either slower than or similar to $\xi_{SC}$ in figures 7.11(b) and (c). Thus we do not find one-to-one correspondence between the behaviour of structural and dynamic correlation lengths.

The fact that different in behaviour between the dynamic and static lengths is found is in agreement with some recent studies on 2D and 3D systems [34–36], however we note that others have found a one-to-one correspondence in the growth in a lengthscale relating to static crystalline order and the dynamic correlation length for polydisperse quasi-hard sphere systems [12–15, 55].

For our systems the order we find in the KA mixture is distinct from the crystalline structure and is thought to frustrate crystallisation. For the Wahnstöm mixture it was thought that static crystalline order might underlie the dynamic heterogeneities [15], however we find below that the majority of the icosahedra present are not compatible with the crystal structure. We note that in the studies on 3D systems that have found one-to-one correspondence between the structural and dynamical lengthscales [15, 55], the relative increase in the static lengthscales going from state points in the Arrhenius regime to into the supercooled regime is no more than a factor of 2. In figure 7.11(b) and (c) our static lengths $\xi_{SC}$ show an increase of the same order between Arrhenius and supercooled state points, however the increase in $\xi_4$ is relatively much greater (factor of $\approx 5$ or more between high and low $T$). We note a recent study that suggests one-to-one correspondence in lengthscales for crystalline order and dynamic heterogeneities on quasi-hard spheres breaks down with the addition of attractions between the particles [56].

We rationalise why different behaviour is seen for $\xi_{SC}$ and $\xi_4$ by considering strength of the correlation between the structured and immobile particles. Figure 7.11(a) shows the correlation between low mobility particles and particles in long-lived 13A clusters ($\tau_f > \tau^{\Delta}_l$). There appears to be reasonable correlation between the immobile and the slow particles, however we note instances of small green dots in the figure indicating structured particles with high mobility over the proceeding $\tau_h$ in the trajectory.

The particle sites at $t = 0$ selected by the overlap function $w$, and hence by $S_4(k, \tau_h)$, all have $\Delta r^2(\tau_h) < 0.09$ strictly. However frequently the structured particles have $\Delta r^2(\tau_h) >$
0.09, as shown in figures 7.6(b) and figures 7.7(b). Therefore although the structured particles display lower mobility than the system-wide average, the correlation between structured and immobile particles is not a perfect one, and therefore it is not guaranteed that the lengthscales will necessarily grow in the same manner.

The structured domains in both liquids form rarefied networks with $d_f \approx 2$. These networks do not fill space, whereas it is thought that the critical-like nature of the dynamic heterogeneities means the domains have $d_f \approx 2.5$ [13, 57]. Therefore geometrically it appears that the domains of slow and structured particles are different, at least at the state points we have accessed. Moreover the number of particles in the domains are unlikely to coincide across a range of temperatures, as the $N_C$ for the structured particles increase monotonically on approaching the glass transition, while the number of particles selected by $Q(t)$ is relatively constant as a function of temperature.

Note $\chi_4$ has been shown to exhibit dependence upon system size for $N \lesssim 1000$ [58]. We expect that such effects are reasonably small here, and have taken care to only consider temperatures where all our measured lengths are smaller than the system size. While system size effects cannot be ruled out, we do not believe these make a significant impact on the conclusions we draw.

The lengthscales $\xi_R$ indicate how the size of the domains grow on cooling. For the lowest temperature Wahnström state point studied, the network of icosahedra percolates, and thus technically the size of the domains can no longer be defined. This might suggest a diverging structural lengthscale at a temperature higher than that inferred from the dynamic correlation length $\xi_4$. Percolating domains of icosahedra do not imply structural arrest since icosahedra have a finite lifetime. This scenario contrasts with colloidal gels where a percolating network of local structures leads to dynamic arrest [59].

Thus the question remains as to the most appropriate structural correlation length to explain the viscous slowing down in supercooled liquids, and how order-specific correlation lengths, such as $\xi_R$ and $\xi_S$, are related to order-agnostic structural correlation lengths [28–30, 34, 39, 60]. We also note that figures 7.8(f) and 7.9(f) strongly indicate that the effect of the domains of clustered particles on the surrounding liquid extends around one particle diameter from the domains. This shows that the dynamical effect of the structured particles is hierarchical and not solely limited to the structured domains themselves. However the correlation lengths we measured from a structure factor of the domains and their first nearest neighbours was no greater then the lengthscale $\xi_S$ for the domains themselves.
Figure 7.12: (a) Relationship between icosahedral 13A domains and the crystalline Frank-Kasper and icosahedral clusters for $T = 0.604$. The number $N_C^*(\tau_\ell \geq t)/N$ is the fraction of particles detected within clusters lifetime $\tau_\ell \geq t$. The dashed line is for Frank-Kasper clusters, and the dotted line is for icosahedral clusters with a $B$-particles in the centre and arrangements of $A$- and $B$-species in the shell of the icosahedron compatible with the bulk crystal phase [22]. Both of these clusters exist in the MgZn$_2$ structure of the Wahnström crystal. The solid line is for all icosahedra, irrespective of the arrangement of $A$- and $B$-species. (b) Snapshot at $T = 0.604$ showing the overlap between icosahedral domains and Frank-Kasper clusters. Green particles are the icosahedral domains, red particles are those in both Frank-Kasper and icosahedral clusters, and black are Frank-Kasper particles not within icosahedral domains. The small blue particles are not members of icosahedral or Frank-Kasper clusters.
7.6. Icosahedral domains and crystalline order in the Wahnström mixture

Pedersen et al. identified that the Wahnström mixture crystallises by phase separation into a crystal with MgZn$_2$ Laves phase, which is formed of 13A icosahedra and Frank-Kasper bonds with specific compositions and arrangements of the A- and B-species, and a liquid of A particles [22, 61]. The icosahedra within the crystal structure are composed of six of the larger A-particles and seven of the smaller B-species. Of all possible arrangements of the A- and B-particles within the icosahedral cluster for this composition, only two occur in the crystal structure.

They suggested that Frank-Kasper clusters, consisting of two A-species particles bonded to six common B-species neighbours, which occur in the crystalline lattice, act to stabilise the supercooled liquid. Here we discuss the relationship between the icosahedral domains we identify and crystalline structure of the supercooled liquid.

In figure 7.12(a) we present data for the fraction of particles detected within clusters of lifetime $\tau_t \geq t$ for three types of cluster. First are for the icosahedral clusters (13A) that form extended domains through the system. These clusters can be made of any number of A- and B-species or arrangement of the species on the shell of the cluster. Second are for icosahedral clusters compatible with the crystal structure [22]. There are two different arrangements that consist of six A-particles and six B-particles arranged around a central B-particle. These are identified by the number of connected B-species in two sets on the shell of the icosahedral cluster that are separated by a ring of six A-particles. One arrangement has two sets of three connected B-particles, and the other one pair and one quadruplet of B-particles. The third cluster is the Frank-Kasper cluster, which consists of a bonded pair of A-species surrounded by a ring of six B-particles.

For all cluster lifetimes there are more particles in icosahedral clusters than in Frank-Kasper or crystal compatible icosahedra. It is strictly necessary that particles in crystal compatible icosahedral clusters are fewer than in icosahedral clusters, as the former are by definition icosahedra themselves. However we emphasise that very few particles (<5% of the system) are identified in the clusters compatible with the crystal for the lowest temperature state point we studied. We find for $T = 0.604$ that 83% of particles in Frank-Kasper clusters lie within the icosahedral domains. The overlap of particles in Frank-Kasper clusters and icosahedral domains is shown in figure 7.12(b).

We note that the lifetime autocorrelation function for the crystalline icosahedra and Frank-Kasper clusters are very slow to decay. The decay is slower than for all icosahedra (figure 7.4(a)). Frank-Kasper clusters are a subset of the 8K cluster. The 8K cluster has an identical structure to the Frank-Kasper cluster, however 8K is free to have any composition and arrangement of A- and B-species. We identify the slowly decaying tail in the
lifetime autocorrelation function of 8K in figure \textit{7.4(a)} with Frank-Kasper clusters.

Only 10\% of the particles within icosahedral domains are members of clusters in the crystal structure. Although an icosahedral structure itself is a key structural motif of the Wahnström crystal, the icosahedral clusters formed in a supercooled liquid are weakly linked to the crystal structure, presumably due to entropic frustration of the chemical arrangement of the species within the cluster.

We conclude that crystalline structuring in supercooled Wahnström liquids is a relatively small component of wider icosahedral ordering. The icosahedral ordering is frequently incompatible with the crystal structure due to the composition, i.e. $n_A$ is frequently not equal to six, cf. figure \textit{7.5(a)}, or because the arrangements of the $A$- and $B$-species within the cluster are inconsistent with that found in the crystal.

\section{7.7. Summary and conclusions}

We have demonstrated that by studying the lifetimes of different structural orderings within the Wahnström and KA supercooled liquids, the relatively stable orderings of particles can be detected unambiguously. This method alleviates some of the difficulties in identifying structural correlations relevant to glassy behaviour from the temperature dependency of the number of particles participating in clusters. The number of particles in clusters can vary continuously within the Arrhenius relaxation regime of liquids \cite{62}, therefore changing local structural on supercooling is not necessarily important for glassy behaviour.

The most stable clusters found in the Wahnström and KA supercooled liquids are the 13A icosahedra and 11A polyhedra respectively. The relaxation of particles within these clusters proceeds more slowly as the lifetime of the cluster lifetimes increase.

In both mixtures the long-lived clusters form rarefied domains on cooling with a fractal dimension $d_f \simeq 2$, i.e. the structured domains are non-spacing filling, at least in the regime we have accessed. For the Wahnström mixture the lifetime of the 13A clusters increases markedly with the size of the domains of 13A clusters that they are part of. The non-icosahedral particles neighbouring these domains have reduced mobility compared to particles further from the domains, suggesting a link between structure and dynamic heterogeneity at this level of detail. This effect, if slightly less pronounced than the Wahnström case, also occurs in the KA mixture with domains of 11A polyhedra.

We examined the relationship between the structured domains and the dynamic heterogeneities by considering static and dynamic correlation lengths of structured/slow particles. A static correlation length calculated in a like-for-like manner with the dynamic correlation length was found to grow moderately on cooling, however its increase was outmatched by the growth in the dynamic correlation length. The difference in be-
haviour of the correlation lengths was rationalised by noting that the structured domains grow in a non-space filling manner, and that the correlation between the structured and slow particles is not perfect. The relationship between our static and dynamic correlation lengths, and other length scales for static order, remains an open question.

We considered the relationship of crystalline domains in the supercooled liquids to the dynamic heterogeneities. For the KA mixture it was noted that crystallisation occurs via phase separation of the two species of particle [42], and that the amount of crystalline order detected at all state points was minimal. For the Wahnström mixture the wide distribution of A- and B-species in the shells of icosahedral clusters means that the number of crystal-compatible 13A clusters is small. It was concluded that crystalline structural ordering in the supercooled phase is a relatively small component of wider icosahedral ordering.

Finally we consider a possible direction for future study. It has been shown recently that the time integral of an order parameter associated with 11A clusters can be used to drive a first order transition in an ensemble of trajectories [63]. The susceptibility of the transition to the field coupled to the time integral of the structural order parameter was found to be higher than when biasing with a field coupled to the dynamical activity, which is the traditional method by which the transition is accessed. Furthermore a recent study by Singh et al. has shown that ultra-stable KA glasses prepared by a vapour deposition technique have high numbers of clusters equivalent to 11A polyhedra [64]. Together these results provide further evidence for a connection between the atomic level structure, most easily accessed with high-order structural correlation functions, and the glass transition.

The biasing of fields coupled to time integrated structural order parameters in trajectory space thus opens up a new route by which ‘ultra-stable’ glassy states can be prepared. The relaxation times inferred for these states are many orders of magnitude higher than what can currently be prepared with conventional simulations. Study and characterisation of the properties of these states will shed further light on nature and role of local structure in the glass transition.
7.8. Bibliography


CHAPTER 8

Structure and Dynamics in Strongly Correlating Liquids

8.1. Introduction

A recent series of papers have investigated the properties of liquids where the fluctuations of the potential energy $U$ and the virial $W$ in constant volume ensembles are correlated [1–5]. In these papers it was proposed that liquids with a high degree of correlation between the fluctuations of $U$ and $W$ obey a number of scaling laws for their static structural, dynamical and thermodynamic properties. Such liquids have been termed ‘strongly correlating’ liquids.

One of the properties displayed by strongly correlating liquids is the existence of ‘isomorphs’ through the phase diagram in regions where the correlation between the $U$ and $W$ fluctuations is strong [4]. Isomorphs are curves through $(\rho, T)$ space along which the structure and dynamics of liquids are invariant, to a good approximation, when written in a set of reduced units [4, 5]. A number of thermodynamic properties, such as the excess entropy and the excess isochoric specific heat, are also found to be invariant between isomorphic state points.

The initial numerical investigations into the invariance of structure and dynamics along isomorphs focused on pair correlations, i.e. $g(r)$ and $F_s(k, t)$ [4]. Here we go one stage further and test the validity of isomorphs using higher order correlation functions for structure and dynamics. The yield of 11A clusters is used as an order parameter for structure, and the lifetime autocorrelation function as an order parameter for the many-particle dynamical correlations along isomorphic curves.

**Inverse power law (IPL)** potentials obey perfect $U$-$W$ correlation and isomorphs in the phase diagram of these systems are exact. A connection is made between strongly correlating liquids with attractions and purely repulsive IPL liquids by the gradient $\gamma$ of a linear fit for a scatter plot of $U$ and $W$ fluctuations. An IPL reference potential with exponent $n = 3 \gamma$ reproduces to a good approximation the pair structure and dynamics for
the full system with attractions at the state point where \( \gamma \) is measured [4, 6]. Moreover for systems with good isomorphs through the phase diagram, it has been conjectured that \( \gamma \) is a density-dependent parameter, i.e. \( \gamma = \gamma(\rho) \), and as such the IPL approximation remains valid along the isopycnic. This conjecture has been shown to break down however for strongly correlating liquids where the potential is truncated at ranges shorter than the mean inter-particle separation [7, 8], or if the correlation between \( U \) and \( W \) drops significantly along the isopycnic such that the liquid is no longer strongly correlating.

Pedersen et al. employed this conjecture to derive a repulsive IPL potential that approximates the attractive Kob-Andersen (KA) Lennard-Jones (LJ) glass former [9]. The IPL system matched the pair structure, dynamics, and fragility of the KA mixture along the \( \rho = 1.2 \) isopycnic. The correspondence between the purely repulsive reference system and the original system with attractions held its validity over a range temperatures from within the Arrhenius liquid regime to deeply supercooled state points. This case therefore presents an opportunity to test the validity of theories that pertain the glass transition is (at least in part) driven by the formation of stable local structures within the supercooled liquid phase.

Here we consider the local structure of the IPL reference system compared to the full KA model using the topological cluster classification (TCC) algorithm. In particular we examine the behaviour of 11A clusters, which were found in chapter 7 to be slowly relaxing structures in the KA supercooled liquid. Moreover the presence and size of domains of 11A clusters has been suggested as a way to rationalise the difference in fragility between the full KA LJ system with attractions and its Weeks-Chandler-Andersen (WCA) counterpart with purely repulsive interactions [10].

We find that there is a substantial difference in the numbers of 11A particles between the KA LJ and IPL reference models, which can be traced back to small differences in the partial radial distribution functions of the two models. The consequences of this result for theories of the glass transition pertaining to the importance of local structuring are discussed in the results and conclusion sections.

8.2. Methods

8.2.1. Strongly correlating liquids

In the canonical \( NVT \)-ensemble virial the pressure is the sum of contributions from ideal gas and interaction terms:

\[
P V = N k_B T + W ,
\]

(8.1)

The virial \( W \) is given by

\[
W(r^N) = -\frac{1}{3} \sum_{i=1}^{N} \sum_{i<j}^{N} r_{ij} u'(r_{ij}) .
\]

(8.2)
Figure 8.1: Scatter plots of the potential $U$ and the virial $W$ (squares) and linear fits (red lines). (a) KA IPL: $\rho = 1.2$, $T = 1.0$, perfect correlation of $U$ and $W$. (b) KA LJ: $\rho = 1.2$, $T = 1.0$, strongly correlating. (c) Monodisperse LJ above the critical point: $\rho = 0.32$, $T = 1.3$, weakly correlating.

The fluctuations of $U$ and $W$ in the ensemble can be represented on a scatter plot, as shown in figure 8.1. The degree of correlation between the variables is characterised by Pearson’s $R$ coefficient

$$R = \frac{\langle \Delta W \Delta U \rangle}{\sqrt{\langle (\Delta W)^2 \rangle \langle (\Delta U)^2 \rangle}},$$  

where $\Delta U = U - \langle U \rangle$ and $\Delta W = W - \langle W \rangle$. Strongly correlating liquids are defined empirically as liquids where $R > 0.9$ [1]. The parameter which defines the ‘slope’ of the correlation is $\gamma$

$$\gamma = \frac{\sqrt{\langle (\Delta W)^2 \rangle}}{\sqrt{\langle (\Delta U)^2 \rangle}}.$$  

The parameters $R$ and $\gamma$ are state point dependent and liquids may demonstrate the strongly correlating property ($R > 0.9$) in some regions of phase space and not in others. In figures 8.1(a) to (c) we show scatter plots of $W/N$ versus $U/N$ for an IPL system, a strongly correlating liquid state point (KA LJ) and a weakly correlating liquid state point (monodisperse LJ) respectively. Perfect correlation is obtained for the IPL liquid as $W = \gamma U$ strictly for IPL potentials.

### 8.2.2. Isomorphs

Isomorphs are curves through strongly correlating regions of the phase diagram along which a number of structural, dynamical and thermodynamic quantities are invariant when presented in a set of reduced units. The theory can be reduced to a single approximation for the relative Boltzmann weights that identical microstates of two isomorphic state points$^1$ contribute to the partition function. Two state points $(\rho_1, T_1)$ and $(\rho_2, T_2)$ are isomorphic if the statistical weights of representative configurations at state

$^1$Isomorphic state points are points on the same isomorph.
point 1 \( r^N_{(1)} \) are proportional to the statistical weights of scaled configurations of state point 1 at state point 2, where the configurations are scaled between the state points as \( r^N_{(2)} = \rho_1^{1/3} r^N_{(1)} / \rho_2^{1/3} \). In other words the following relationship holds [4]:

\[
e^{-U(r^N_{(1)})/k_B T_1} = C_{12} e^{-U(r^N_{(2)})/k_B T_2}.
\]

(8.5)

The parameter \( C_{12} \) only depends on the state points 1 and 2 and not on the details of the microscopic configurations.

The theory of isomorphs is rigorous when \( C_{12} = 1 \), which only occurs for IPL potentials. For other potentials the isomorphs are approximate, where the strength of the approximation depends on how close \( R \) is to unity between state points on an isomorphic curve.

The consequence of equation 8.5 is that a number of quantities measured along isomorphs can be collapsed when cast in terms of reduced units for energy \((k_B T)\), length \((\rho^{-1/3})\) and time \((\sqrt{m/k_B T} \rho^{-2/3})\) for Newtonian dynamics. As the microstates of isomorphic state points scale trivially onto each other, all structural measurements are invariant to a good approximation. Newtonian dynamics in reduced time are invariant between isomorphic state points as long as the timescale of the thermostat is adjusted to be invariant between the state points. Invariant thermodynamic properties along isomorphs include the excess entropy, the configurational entropy and the isochoric specific heat [4].

The shape of isomorphic curves can be calculated for potentials that are the sum of IPLs using the method outlined in reference [11]. For LJ potentials, as employed by the KA model, a scaling function is defined relative to a reference state point for the isomorph with \((\rho^*, T^*)\) and \(\gamma^*\). The scaling function \( h(\tilde{\rho}) \) is

\[
h(\tilde{\rho}) = \tilde{\rho}^4 (\gamma^*/2 - 1) - \tilde{\rho}^2 (\gamma^*/2 - 2),
\]

(8.6)

where \( \tilde{\rho} = \rho/\rho^* \). The number \( h(\tilde{\rho})/T \) is constant along isomorphs meaning that all state points along an isomorph can then be calculated from the value of \( h(\tilde{\rho})/T \) at the reference state point reference state point, i.e. \( h(\tilde{\rho})/T = h(1)/T^* \).

**8.2.3. Simulation details**

We consider the isomorphs of the KA LJ mixture and its reference KA IPL system defined in reference [9] in 3D molecular dynamics (MD) simulations with periodic boundary conditions (PBCs). The IPL potential is

\[
u_{\alpha\beta}(r) = A \varepsilon_{\alpha\beta} \left( \frac{\sigma_{\alpha\beta}}{r} \right)^{3\gamma},
\]

(8.7)
where the parameters $A = 1.9341$ and $\gamma = 5.16$ are calculated from our simulations. The values of $\gamma$ and $A$ are calculated from gradients of scatter plots of the LJ virial versus the LJ potential, and the LJ potential versus IPL potential without the $A$ prefactor for the state points $\rho^* = 1.2$ and $T^*$ values of 0.5, 0.525, 0.6, 0.75, 1.0 and 2.0.

We truncate and shift both LJ and IPL potentials at $2.5\sigma_{\alpha\beta}$ and simulate in the $NVT$-ensemble a system of $N = 1000$ particles, $N_A = 800$. The temperature is controlled using the Nosé-Hoover (NH) thermostat with $\tau_{NH} = 0.03$. The values of $\tau_{NH}$ are adjusted along the isomorphs such that they are identical when reduced by $\sqrt{m/k_B T \rho^{2/3}}$. The initial configuration at $\rho = 1.2$, $T = 2.0$ is an face-centred cubic (FCC) crystal which is melted and the liquid equilibrated before trajectories are sampled. Each lower temperature state point is thoroughly equilibrated after an instantaneous quench from the previous higher $T$ state point. The trajectories sampled for each state point are $300\tau^A$ long.

We consider six isomorphs for both the KA LJ and KA IPL models, where the reference state points are $\rho^* = 1.2$ with $T^* = 0.5, 0.525, 0.6, 0.75, 1.0$ and 2.0. The initial configuration for a new state point along an isomorph is obtained by scaling the positions and velocities from a configuration of the reference state point, using $r_i = (\rho^*)^{1/3} r_i^*/\rho^{1/3}$ and $v_i = T^{1/2} v_i^*(T^*)^{1/2}$. The new state point is equilibrated before sampling a $300\tau^A$ trajectory. We traverse out isomorphs from $\rho^* = 1.2$ between $\rho = [1.0, 2.0]$. The $\rho = 1.0$ state points for the KA LJ model crystallise on all isomorphs except $\rho^* = 1.2$, $T^* = 2.0$, indicating that the crystallisation time along isomorphs is not invariant.

In figure 8.2(a) we show the correlation coefficient $R$ for the $U\cdot W$ fluctuations in the KA LJ mixture. As the temperature decreases the value of $R$ decreases. In figure 8.2(b) the shape of the isomorphic curves in the phase diagram are shown, as calculated using equation 8.6.
8.3. Results

8.3.1. Structure and dynamics across isomorphic state points

We begin by analysing the structure and dynamics along the isomorphs for the KA IPL system. In figure 8.3(a) the number of particles detected within 11A clusters along three different isomorphs for the KA IPL system is shown. The isomorphs for this system are exact and hence $N_{11A}/N$ is identical across all state points along an isomorph, within the statistical limits of the data. The lifetime autocorrelation functions for the 11A cluster all collapse once the data have been normalised by $\tau_\alpha^A$. These results demonstrate that higher order correlations in structure and dynamics are invariant along isomorphs in IPL systems, as expected.

We move on to the full KA LJ system where structure and dynamics are expected to be invariant along isomorphs to a good approximation. As figures 8.4(a) and (b) show, there are in fact continuous changes in $N_{11A}/N$ and $P_{11A}^*(\tau \geq t)$ between isomorphic state points. The relative differences in these quantities between isomorphic state points is larger than the relative differences in two-body static and dynamic correlation functions $g(r)$ and $F_s(k_p,t)$, cf. reference [4]. The relative differences in $N_{11A}/N$ between isomorphic state points increase as the temperature is lowered, corresponding to the decrease in $R$ with $1/T$ and the weakening of the isomorphic approximation.

The results of figure 8.4 indicate that higher-order measures for structure and dynamics, such as our analysis of particle clustering, are more sensitive to the bounds of validity of the isomorphic approximation than two-body correlation functions for the structure and dynamics.
8.3.2. Comparison of the purely repulsive system to the full LJ system

In this section we compare structural and dynamical features of the KA LJ system and its purely repulsive IPL reference system.

In figures 8.5(a)-(c) we compare the partial radial distribution functions for the systems with and without attractions. The partial radial distribution functions are broadly similar between the two models. The largest differences are seen for $g_{BB}(r)$, and around the first of peak of $g_{AB}(r)$. We note that the radial distribution functions from the IPL model are a better match to those for the full LJ system than to partial $g(r)$’s from the WCA variant of the LJ system [9].

We proceed to consider the dynamics in the two systems by plotting the self self-intermediate scattering function (ISF) for the A particles $F_s^A(k_p,t)$ and the dynamic susceptibility $\chi_4$ in figures 8.6(a) and (b). The ISFs are well matched between the two mod-
els, and consequently the fragility and degree of super-Arrhenius behaviour in relaxation times are similar. The dynamic susceptibilities are also well matched indicating that the degree of cooperativity in the relaxation dynamics are comparable between the models. This scenario contrasts with the WCA approximation for the KA mixture, where the viscous behaviour is found to be significantly different between the two models [12]. The difference between the relaxation dynamics of the KA LJ and KA WCA models has been attributed to the numbers and spatial extent of 11A polyhedra\(^2\) in the supercooled regime [10].

In figures 8.7(a) and (b) the fraction of particles found in 11A clusters and the lifetime autocorrelation function for the 11A clusters are shown. Figure 8.7(a) clearly shows that

\(^2\)The TCC 11A cluster is equivalent to the Voronoi face analysis (VFA) (0,2,8) cluster identified in reference [10].

Figure 8.6: The dynamics of the KA LJ and IPL variants. The (a) ISF \(F_s^A(k_p, t)\) and (b) dynamic susceptibility \(\chi_4\). Data for \(\chi_4\) at the lowest temperature state point \((T = 0.5)\) is excluded due to the finite size of the simulations.

Figure 8.7: Analysis of the statistics and dynamics of 11A clusters in the KA LJ and KA IPL mixtures. (a) \(N_{11A}/N\) and (b) \(P_{11A}^{\tau}(\tau_t \geq t)\).
there are significant differences in the number of particles participating in 11A clusters between the two models. A consequence of this result is that the size and spatial extent of 11A domains are likely to be different between the two models. Figure 8.7(b) shows that the lifetimes of 11A clusters also differ between the KA LJ model and its IPL reference system.

The difference in numbers of particles participating in 11A clusters between the two models may be traced back to subtle deviations in the partial radial distribution functions (figure 8.5). The $AB$ partial radial distribution function shows are more pronounced first peak for the KA LJ mixture than the IPL reference system (figure 8.5(b)). Conversely the $B$ particles in the KA LJ model appear to have a lower affinity for bonds with other $B$-particles compared to the IPL counterpart (lower first peak in figure 8.5(c)). Both these deviations are consistent with a larger number of 11A clusters in the KA LJ model, as 11A clusters contain a central $B$-particle surrounded by large numbers of $A$-species and is a stable local arrangement of the particles.

8.4. Discussion

These results raise a number of questions about the relationship between local structuring and glassy behaviour. The non-perturbative effect of attractions on the viscous behaviour between the KA LJ and KA WCA model was rationalised by some by differences in higher-order structural correlations between the two systems [10]. However here we have shown that the repulsive IPL system, which matches the static and dynamic pair-correlations of the KA LJ system, displays markedly different behaviour in terms of the static numbers and persistence of 11A clusters. This structure was suggested to be a proxy for higher-order structural correlations that may be necessary for inclusion in theories of the glass transition in order that the predictions of the relaxation times are accurate for both the KA LJ and KA WCA models [7, 10]. However here we find two similar models - KA LJ and KA IPL - where the composition, interactions, pair-structure, fragility and relaxation times are quantitatively similar, yet the proxy for higher-order structural correlations that was considered shows large deviations.

It is possible to construct an argument that the difference in behaviour of 11A clusters between the IPL and full LJ model is not necessarily significant. We have not examined the temperature behaviour of other clusters in the IPL model, or performed a systematic analysis of the lifetimes of the TCC clusters to identify the most stable local arrangement. Therefore we cannot rule out the existence of another type of cluster with longer lifetimes and similar prevalence to the 11A clusters in the KA IPL mixture.

It might also be argued for the temperature regime accessed in these simulations that mode-coupling effects are important in determining the relaxation times, and their
effects cannot be discounted [13]. However the mode-coupling approach in its original formulation was unable to describe the difference in relaxation behaviour of the KA LJ and WCA models [14].

A third argument that could reasonably be made is that the coincidence in relaxation times of the IPL and the full KA LJ may break down at lower temperatures. Figure 8.2(a) showed that the correlation coefficient for $U-W$ fluctuations drops on decreasing temperature, therefore it is conceivable that the results of the IPL reference potential may deviate from the low $T$ behaviour in the KA LJ model. Indeed we note the values of $\gamma$ obtained from state points along the $\rho = 1.2$ isopycnic differ slightly, indicating that a single IPL potential may not be appropriate to model the entire temperature range of the supercooled liquid as was the case here.

If the true explanation is one of the arguments proposed, it appears that the importance of local structures for the glass transition is more complicated than may previously have been thought. If another cluster with a stronger connection to slow dynamics than 11A cannot be identified, our results suggest that it is not appropriate to write the relaxation time in both these models as a single function of the participation number in 11A clusters (or a correlation length from the 11A domains) and the fragility, as was suggested with crystalline clusters in polydisperse quasi-hard sphere models [15]. Moreover it provides evidence to support the position considered in chapter 7 that higher-order structural changes in supercooled liquids are unimportant features for the glass transition, as large changes in the numbers of clusters occur in the equilibrium liquid as well.

Further evidence against the significance of 11A clusters appears in figure 8.4(a). The fraction of particles in 11A clusters is not constant along KA LJ isomorphs, whereas the reduced relaxation times only show relatively smaller deviations from each other [4].

To settle some these issues raised it is necessary to perform a more detailed study of the behaviour of higher-order structural correlation functions in the KA IPL mixture. It would also be beneficial to consider the lower temperature behaviour of the KA LJ model and its IPL counterpart to see how the viscous dynamics develop in each case.

### 8.5. Conclusions

In this chapter we have considered the behaviour of structural correlations in a strongly correlating liquid. It was demonstrated with measurement of the statistics and dynamics of 11A clusters along isomorphs of the KA LJ that higher-order structural and dynamical correlations show larger deviations from each other along isomorphs than two-body correlations. This result is at odds with the invariance of structure in reduced units predicted by the theory of isomorphs. The size of the deviations in the higher-order structural correlation functions between isomorphic state points increase as $R$ decreases on
cooling.

The temperature behaviour of 11A clusters in the KA LJ model was compared with its IPL reference potential. Significant deviations were found in both the fraction of particles participating in 11A clusters and the lifetime of 11A clusters, indicating that differences in the higher-order structural and dynamic correlations do not necessarily translate to differences in relaxation times. It remains an open question as to the importance of 11A clusters in determining the glassy behaviour of the KA LJ and KA IPL models. However our results suggest that the glassy dynamics in both of these models are not solely determined by the prevalence of 11A clusters. Further investigation into higher-order correlation functions in the KA IPL model is recommended to clarify the relationship between relaxation times and higher-order structural correlations.
8.6. Bibliography


Conclusions and Outlook

9.1. On the Frank conjecture and the TCC algorithm

In this thesis we have examined the types of local structures formed by particles in a range of systems. The method used to identify local structures searches for clusters of particles equivalent to the ground state clusters formed by small numbers of particles interacting in isolation. The method is a generalisation to structures of varying numbers of particles of a conjecture posed by Sir Charles Frank in 1952 [1]. Frank proposed that supercooled Lennard-Jones (LJ) liquids would be characterised by thirteen particle icosahedral structures in preference to face-centred cubic (FCC) or hexagonal close packed (HCP) crystal arrangements, as in isolation icosahedral clusters minimise the energy of the interactions.

Our results on colloidal clusters and supercooled liquids have shown that this conjecture does not hold in general, as a number of instances were found where the ground state clusters occur with lower frequency than other clusters with the same number of particles. In the case of assembling colloidal clusters (chapter 4) where it might have been expected that the ground state clusters are more prevalent under thermal conditions due to the absence of bulk forces acting upon the clusters, it was demonstrated that for the case of six colloidal particles that entropic contributions to the free energy must be included in order to correctly predict the structures that form. Under non-equilibrium conditions where ergodicity breaking prevents the system sampling all configurations, it was shown that the aggregation sequence of the colloids determines the structures that form, rather than the ground state clusters which are energetically favoured as $T \to 0$.

In conclusion our results provide further evidence that the original conjecture posed by Frank is falsifiable [2–4]. There are however a number of more modern theories that relate glassy behaviour with local structure [5, 6] and hence methods to identify structure in bulk systems are still relevant. In terms of the topological cluster classification (TCC) algorithm, it is recommended that in future its association at a fundamental level with
the Frank conjecture is deemphasised.

The review of structural detection methods in chapter 3 highlighted that there are relatively few methods with the capability to identify local structures with a range of sizes. This is one of the strengths of the TCC algorithm. It is therefore suggested that the TCC algorithm is developed in a direction that allows different structures with \( m \) particles to be identified in a more systematic manner than is currently the case, i.e. the structures identified are the ground state clusters of a disparate range of interaction potentials. This could be achieved by appealing to the different rigid packings of hard spheres [7], classifying the various local minima in the potential energy landscape of isolated clusters into groups representing different structures, or by identifying structures across the local minima of an effective energy consisting of particle interaction terms and a mean-field term representing the influence of an external bulk that the particles are embedded within [8].

### 9.2. Self-assembly of colloidal clusters

Self-assembly processes are becoming increasingly important in the fields of nanosciences and biotechnologies due to the advances being made in the experimental sciences for the synthesis of colloidal and nanoscale particles, and the types of interactions between them. In chapter 4 we studied the self-assembly of colloidal clusters in simulations and compared our results to an experimental colloid-polymer system. We found a narrow range of attraction strengths for which clusters would form and the free energy minimum states would be reached. If the attractions were too weak clusters would either not form, or a superposition of disordered or weakly-bound states would be obtained. If the attraction strengths were too high the system risked become kinetically trapped in a higher energy state which was arrived at as a consequence of the aggregation sequence of the particles.

After considering isolated clusters, we proceeded to consider the effect that electrostatic interactions between the clusters have on the intra-cluster structure. By varying the repulsion strength and the density in simulations of an ensemble of clusters, we demonstrated that the yield of clusters is perturbed by the inter-cluster interactions under certain conditions. For simulations at low density and with weak charging, the yield of structures closely matched what was found for the isolated clusters. The effect of increasing the density or the strength of the electrostatic repulsions between clusters at low colloidal attraction strengths was to increase the yield of clusters with compact structure. This effect is due to the pressure between the clusters mediated by the electrostatics, and demonstrates that it may not always be appropriate to consider the clusters in a cluster fluid as if each were an isolated system.
The variety and complexity of structures formed by the self-assembly of colloids with spherical attractions indicates that self-assembly processes need to be carefully designed in order to obtain high yields of a desired product. This can be achieved with design for the shape of the nanoparticles [9] and the types of interactions between them, either with directional, geometrical or chemical binding sites [10, 11]. We also note recent studies that suggest yields are maximised if microscopic reversibility holds in the self-assembly process [12]. We infer that computer simulations will play an important role in the design and engineering of self-assembly processes, as the parameter space can be mapped quickly and efficiently given the small system sizes and relative simplicity of simulations for self-assembling nanosystems.

9.3. Structure at interfaces

In chapter 5 we studied the structure at liquid-gas interfaces in Monte Carlo (MC) simulations. The TCC algorithm was used to identify the number of particles participating in potential energy minimum clusters as a function of distance from the interface. The fraction of particles participating within the clusters was found to monotonically decrease in the interfacial region between the liquid and the gas.

The main effect of the interface on the liquid structure was seen in terms of the orientations taken by elongated clusters. Two types of cluster were found to align with their longest dimensions parallel to the interface, demonstrating that the presence of the interface perturbs the orientations that local structures adopt near to the free surface. The strength of this effect increases as the liquids are cooled and the interfacial tension increases. For state points where interfacial layering propagates into the bulk liquid, elongated clusters are found to orientate to a certain degree in order to maximise the number of particles within the high density layers. This effect extends to about four particle diameters into the liquid for the lowest temperature state point accessible in the models that we studied.

We note previous results suggesting that five-fold symmetric order lying parallel to liquid-crystal interfaces is promoted as the interface is approached [13, 14]. As an option for future study we suggest testing this result directly by considering the orientation of sp5 rings detected with the TCC algorithm near to a liquid-crystal interface.

9.4. Dynamics of clusters

In chapter 6 we developed methods to identify the lifetime that clusters persist in simulations of colloidal clusters and supercooled liquids. The methods reveal the nature of the dynamics of local structures in these systems.

A method was devised to identify and distinguish different instances of clusters that
form in a trajectory. The method employs the indices of the particles, the type of TCC cluster that is detected, and to a certain extent the arrangement of the particles within the cluster to distinguish individual instances of clusters. This method allows different instances of clusters to be tracked within a trajectory and persistence lifetimes to be defined.

For the simulations of six colloids in isolation forming 6A or 6Z clusters, it was shown that the lifetimes for instances of each structure are comparable. This result indicates that the typical energy barriers to rearrange from either of these states are similar. In order to maintain the equilibrium ratio of 6Z to 6A clusters in the configurations, it was inferred that 6Z to 6Z transitions are at least 22 times more frequent than 6Z to 6A transitions.

For the colloidal interactions studied, the fluctuations of the particles around the sites within 6A and 6Z clusters are small compared to the fluctuations that typically occur in LJ systems such the Wahnstöm and Kob-Andersen (KA) binary mixtures. The microscopic fluctuations in the LJ supercooled liquids are found to cause fluctuations in the bond network on timescales comparable to ballistic motion and the beta-regime for relaxation. A timescale was introduced by which discrete periods where an instance is detected can be joined together in order to yield more physically relevant lifetimes.

The tool of choice for analysing the lifetimes of clusters was the lifetime autocorrelation function, which represents the fraction of clusters with lifetimes longer than a given time. For two model supercooled liquids studied in chapter 7 the lifetime autocorrelation functions showed that the majority of clusters have lifetimes shorter than $0.1 \tau_\alpha^A$ at deeply supercooled state points. The exact reasons as to why large numbers of clusters have such short lifetimes compared to the relaxation time $\tau_\alpha^A$ remain unclear. The consequences of this result appear somewhat less significant when one considers the number of particles that participate in clusters of a certain lifetime or greater. As clusters may overlap, particles are frequently members of more than one cluster with a given structure, and a more significant fraction of the particles are found within clusters with lifetimes commensurate to or greater than $\tau_\alpha^A$.

In order to gain a better understanding of the lifetimes of clusters, research is needed into the processes by which one structure breaks up and another is formed. In particular it would be useful to characterise the typical displacement of particles when a structure dissolves: is it comparable to the size of fluctuations within the cage, or comparable to the size of the displacements that occur as cages reorder (i.e. when cage hopping occurs)? Another complementary line of research could examine the structural relationships between the clusters that occur between periods where another type of cluster goes undetected. Answers to these questions are important for theories that pertain to a relationship between local structuring and the viscous slowdown in glass-formers, as local structures
need to have lifetimes comparable to dynamically slow regions if they are involved with the dynamic heterogeneities that develop on cooling.

### 9.5. Structure and the glass transition

In chapters 7 and 8 we considered how local structures within two model supercooled liquids are related to the glassy behaviour of each system. We demonstrated that by analysing the lifetime autocorrelation functions of clusters at supercooled state points, stable local structures can be identified unambiguously. Using this method alleviates some of the difficulties in determining relevant structures for glassy behaviour based on the temperature dependency of the clustering, as changes in clustering are displayed continuously across a wide range of temperatures and even within the region of Arrhenius relaxation dynamics.

Particles identified initially within stable clusters in the Wahnström and KA mixtures display retarded mean-square displacements (MSDs) relative to the system-wide average. As the lifetime of the clusters increases the more retarded the MSDs become. On cooling the clusters form domains with fractal dimension $d_f \approx 2$. The larger the domains, the longer the lifetimes of the clusters that constitute the domains. Particles immediately neighbouring the clustered domains have dynamics that are perturbed by the presence of the domains, suggesting a link with dynamic heterogeneities.

We characterised the structured domains and domains of immobile particles within the dynamic heterogeneities by extracting correlation lengths from structure factors for the particles involved within these domains. Both correlation lengths increase on cooling, but the behaviour of the two lengthscales are quite different: the dynamic correlation length grows more markedly than the structural correlation length on cooling. Measuring structural correlation lengths from domains constituted of other types of stable clusters, or from domains of stable clusters and the immediately neighbouring particles, failed to yield a structural correlation length that grows in a one-to-one manner with the dynamic correlation length.

We proposed that difference in behaviour of the lengthscales is attributable to the difference in geometry of the domains, the difference in temperature dependency of the structured and immobile particles, and the quality of the correlation between the structured and slow particles. The exact relationship between these lengthscales and order-agnostic static lengthscales within supercooled liquids remains an open question.

In chapter 8 we considered the behaviour of 11A clusters in the KA system along isomorphic curves in the phase diagram. The fraction of particles identified within 11A clusters, acting as a proxy for higher-order structural correlations, was shown to be more sensitive than two-body correlations for structure to the fact that isomorphs are only
approximations in LJ systems. We considered the yield and temporal stability of 11A clusters between the KA LJ system and a repulsive inverse power law (IPL) reference potential. The reference potential reproduces the pair structure and viscous dynamics of the full KA LJ system, however large deviations were found for the participation of particles within 11A clusters and the stability of the clusters. This result may indicate that the non-Arrhenius relaxation behaviour seen in fragile glass formers is not solely attributable to local structuring, however a more detailed study of the structure in the IPL system with higher-order correlations is needed in order to confirm this conclusion.

A number of questions thus remain about the relationship between structure and the glass transition. Some theories have proposed that the local structuring in supercooled liquids is instrumental for the glass transition [5, 6]. Others have proposed a thermodynamic origin associated with the vanishing of the configuration entropy [15], or purely dynamic origins [16, 17] for the glass transition, where local structuring is either a secondary effect or not considered as significant for the transition.

Our results unambiguously demonstrate that the numbers of particles identified within certain types of cluster change significantly on approaching the glass transition, and the structured domains of these particles are associated with dynamic heterogeneities, at least to a certain extent. Issues that remain to be determined include the relationship between static and dynamic correlation lengths, and the consequence of the difference in structure between the KA LJ and IPL systems which show similar glassy dynamics.

Novel methods for sampling glassy states - by accessing a first-order transition in trajectory space [18] or by vapour deposition [19] - have demonstrated that the structural changes of 11A polyhedra in the KA LJ mixture continue as the dynamics become further arrested. We encourage further studies to be conducted to see whether there is an underlying thermodynamic liquid to liquid or liquid to amorphous solid transition associated with the population of 11A clusters at low temperatures in KA LJ model. We also encourage studies to be conducted into the structural differences between the supercooled liquid and glass accessed by pinning transitions [20, 21]. Such studies will help elucidate the role played by local structuring in the glass transition.
9.6. Bibliography


APPENDIX A

The TCC Clusters

This appendix contains further details on the clusters detected by the topological cluster classification (TCC) algorithm and the structural relationships between them. Figures A.1 and A.2 contain renderings of all the clusters detected by the TCC algorithm. The configuration for each cluster is generated by the reference potential listed in Table 3.2 of chapter 3. Spindle, ring and additional particles, and short-path rings are coloured to highlight the way in which the cluster is identified.

Tables A.1 to A.5 list the ground state clusters for the model systems employed within this thesis. The total binding energy of the particles in the cluster is $E$. The binding energies $E$ listed in tables A.1 to A.5 are reduced by the well depths $\varepsilon$ of the potentials ($\varepsilon_{AA}$ for the binary mixtures).

Figure A.3 summaries how each compound cluster is detected in terms of sub-clusters by the TCC algorithm. The flow diagram indicates the types and numbers of sub-clusters utilised in the detection routine.

For each cluster it is common that a number of sub-clusters exist within the reference configuration. Table A.6 lists the sub-clusters for each cluster. For compound clusters some of these sub-clusters will be used in the detection routine for the cluster. If the cluster is detected in a thermal system, the other sub-clusters identified within the reference configuration should also be expected. The consequence of this is that clusters of different sizes identified by the TCC are not mutually exclusive in that

Cluster binding energies $E$ are reduced by the respective well depths $\varepsilon$ for each potential.
Figure A.1: The clusters with $m = 3$ to $m = 10$ particles. Colours of particles and rings are as the description of the TCC algorithm in Chapter 3.
Appendix A. The TCC Clusters

Figure A.2: The clusters with $m = 11$ to $m = 13$ particles, and the clusters from crystal lattices.
Table A.1: The ground state clusters of the Morse model for various ranges of attraction $\rho_0$. The cluster symbol (CS) and PG (in Schönflies notation) is listed for each cluster. Binding energies $E$ are calculated for mechanically stable clusters in the case that $\rho_0 = 6$. The maximum range for which each cluster is the global minimum is $\rho_{max}$. Data from references [1, 2]. Morse clusters 11D and 12C [1] are omitted as they are not differentiated from 11C and 12B respectively by the TCC algorithm. \(^\dagger\) 11B is not mechanically stable for $\rho_0 = 6$.

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### Table A.2: The ground state clusters of the Lennard-Jones (LJ) model, with cluster symbols (CS) chosen according to their topologically equivalent Morse cluster counterparts. Data reproduced from [2, 3].

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### Table A.3: The ground state clusters of the Chacón-Reinaldo-Falagán-Velasco-Tarazona (CRVT) model, with cluster symbols (CS) chosen according to their topologically equivalent Morse cluster counterparts. Results obtained using GMIN software [4].

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Table A.4: The ground state clusters of the Wahnström mixture in TCC notation for \( m = 5 \) to 13 particles containing \( m_A \) \( A \)-species particles. Clusters highlighted in \textbf{bold} are the lowest energy states for a given value of \( m \). The ground state clusters with \( m_A = 0 \) and \( m_A = m \) are the LJ clusters (table A.2). Results obtained using \textsc{GMIN} software [4].
### Appendix A. The TCC Clusters

#### Table A.5: The ground state clusters of the Kob-Andersen (KA) mixture in TCC notation for \( m = 5 \) to \( 13 \) particles where \( m_A \) is the number of A-species particles. Clusters highlighted in **bold** are the lowest energy states for a given value of \( m \). The ground state clusters with \( m_A = 0 \) and \( m_A = m \) are the LJ clusters (table A.2). Cluster detection with TCC is using the modified Voronoi method with \( f_c = 1.0 \). Results obtained using GMIN software [4].

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Table A.5: The ground state clusters of the Kob-Andersen (KA) mixture in TCC notation for \( m = 5 \) to \( 13 \) particles where \( m_A \) is the number of A-species particles. Clusters highlighted in **bold** are the lowest energy states for a given value of \( m \). The ground state clusters with \( m_A = 0 \) and \( m_A = m \) are the LJ clusters (table A.2). Cluster detection with TCC is using the modified Voronoi method with \( f_c = 1.0 \). Results obtained using GMIN software [4].
Figure A.3: Flow diagrams showing the sub-clusters used in the detection algorithms for each cluster. The number of arrows between clusters indicates the number of distinct sub-clusters used to detect the larger cluster. (a) Compound clusters formed from basic clusters with sp3 and sp4 rings. (b) Compound clusters formed from sp5 ring basic clusters.
Figure A.4: Venn diagram showing the structural relationship between clusters and three-, four- and five-membered shortest path rings. The shortest-path rings are detected within the reference configuration for each cluster (see TCC methodology in chapter 3).
### CS Sub-clusters

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Table A.6: Sub-clusters found in the reference configuration of each cluster. If a cluster is identified in a thermal system, its sub-clusters are also expected to be found based on the hierarchy of other clusters within the reference configuration (it is strictly necessary that the sub-clusters used in the TCC detection routine for the cluster are also found in the thermal system).
A.1. Bibliography


Mapping attractive potentials

B.1. The extended law of corresponding states

The Noro-Frenkel extended law of corresponding states provides a means to calculate the range of an attractive pairwise potential in terms of the range of a square-well potential [1]. The square well potential reads

\[ u_{SW}(r) = \begin{cases} \infty & \text{for } r \leq \sigma, \\ -\epsilon & \text{for } \sigma < r \leq \lambda \sigma, \\ 0 & \text{for } r > \lambda \sigma, \end{cases} \]  

(B.1)

and is a function of three variables. The length \( \sigma \) defines the diameter for the hard-core interaction, \( \lambda \) defines the length of the square-well attraction and \( \epsilon \) is the strength of the attraction or the well-depth.

An attractive potential \( u(r) \) is mapped onto a square-well potential by three scaling parameters that are calculated as functions of \( u(r) \) and \( T \) only, namely \( \epsilon, \sigma_{\text{eff}} \) and \( B^*_2 \). The parameter \( \epsilon \) is chosen as the well-depth of \( u(r) \), i.e. \( -u(r_{\text{min}}) \) where \( r_{\text{min}} \) is the minimum of the potential.

The length scale \( \sigma_{\text{eff}} \) is known as the ‘effective’ hard-sphere diameter for \( u(r) \) and is calculated by first splitting \( u(r) = u_{\text{att}}(r) + u_{\text{rep}}(r) \) into attractive \( u_{\text{att}}(r) \) and repulsive \( u_{\text{rep}}(r) \) components according to the Weeks-Chandler-Andersen (WCA) method [2]:

\[ u_{\text{rep}}(r) = \begin{cases} u(r) + \epsilon & \text{for } r \leq r_{\text{min}}, \\ 0 & \text{for } r > r_{\text{min}}, \end{cases} \]  

(B.2)

and

\[ u_{\text{att}}(r) = \begin{cases} -\epsilon & \text{for } r \leq r_{\text{min}}, \\ u(r) & \text{for } r > r_{\text{min}}, \end{cases} \]  

(B.3)
The effective hard-sphere diameter is then given by the Barker-Henderson expression [3]:

$$\sigma_{\text{eff}} = \int_0^\infty [1 - e^{-u_{\text{rep}}(r)/k_B T}] dr. \quad (B.4)$$

The final parameter $B_2^*$ is called the reduced second virial coefficient and it quantifies the effective range of the attraction of $u(r)$. It is calculated from the second virial coefficient

$$B_2 = 2\pi \int_0^\infty r^2 [1 - e^{-u(r)/k_B T}] dr, \quad (B.5)$$
as

$$B_2^* = \frac{B_2}{2/3\pi \sigma_{\text{eff}}^3}. \quad (B.6)$$

The reduced second virial coefficient is related to the range of the square-well potential $\lambda$ as

$$\lambda = \left(\frac{1 - B_2^*}{\exp(\epsilon/k_B T) - 1} + 1\right)^{1/3}. \quad (B.7)$$

We note that $\epsilon$, $\sigma_{\text{eff}}$ and $B_2^*$ are independent of the density $\rho$ and thus the mapping for $u(r)$ onto the square-well potential is general for all state points at temperature $T$. However any changes to $T$ affect both $\sigma_{\text{eff}}$ and $B_2^*$, so in principle the square-well approximation should be recalculated.

The consequence of the extended law of corresponding states is that liquid-vapour and solid-fluid coexistence lines for the attractive potential can be estimated given knowledge of the square-well phase diagram. Phase points $(\rho, T)$ in the attractive potential plane are related to those the square-well plane via the reduced variables $(\rho^* = \rho \sigma_{\text{eff}}^3, T^* = k_B T/\epsilon)$.

**B.2. Mapping between attractive potentials**

In chapter 4 the extended law of corresponding states is used to calculate a Morse potential approximation for the Asakura-Oosawa (AO) potential. A representative state point is chosen and the extended law of corresponding states is used to calculate $(\epsilon, \sigma_{\text{eff}}, B_2^*)$ from the AO potential. These three parameters define a square-well approximation for the AO potential. The square-well potential is mapped back to a Morse potential by setting Morse energy parameter $\epsilon_M = \epsilon$ and numerically adjusting $\sigma_M$ and $\rho_0$ to yield the required values for $(\sigma_{\text{eff}}, B_2^*)$.

Full details of the experimental colloid-polymer mixture modeled in chapter 4 are given in [4] and are summarised here for completeness. The colloids are made from poly(methyl methacrylate) (PMMA) stabilized with poly hydroxyl steric acid and labeled with fluorescent rhodamine dye. The depletents are polystyrene polymers and the solvent composition is approximately 0.373 cis decalin, 0.093 cyclohexyl bromide and 0.533
tetrachloroethylene by mass.

A typical polymer volume fraction of $\phi_p = 0.78$ and polymer-colloid size ratio of $q = 0.22$ yields an AO potential with attractive strength $\beta \varepsilon_{AO} = 6.0$. For 2 µm colloids the effective hard-sphere diameter is $\sigma_{\text{eff}} = \sigma_{AO} = 2.0$ µm and $B_2^* = -29.4$. Matching the attractive strengths $\beta \varepsilon_M = \beta \varepsilon_{AO}$ and tuning the Morse parameters numerically to match $\sigma_{\text{eff}}$ and $B_2^*$ yields $\sigma_M = 2.01$ µm and $\rho_0 = 16.4$ Mm$^{-1}$. In reduced units these quantities are $\sigma_M = 1$ and $\rho_0 = 33.06$.

The mapping is calculated for a single reference state point. Any changes to the attractions in the experimental system strictly requires a new mapping to a Morse potential. However, over the attractive range considered the variations in $\sigma_M$ and $\rho_0$ are small and $\sigma_M$ and $\rho_0$ are fixed to the values above for all attractive strengths considered.
B.3. Bibliography


APPENDIX C

Frequency of 6A and 6Z colloidal clusters

C.1. Partition function

In order to estimate the relative yields of the 6A and 6Z colloidal clusters studied in chapter 4, we calculate the contribution of the states of each structure to the partition function. From these contributions we can find the relative probability of each of the two states.

The classical partition function for the canonical ensemble (chapter 2, equation 2.17) is approximated as

$$Q_{NVT} = \frac{1}{\Lambda^{3N}N!}Z_t Z_r Z_v,$$

(C.1)

The quantities $Z_t$, $Z_r$ and $Z_v$ are the translational, rotational and vibrational contributions to the partition function respectively, and $\Lambda$ is the de Broglie wavelength containing the kinetic contributions to $Q_{NVT}$:

$$\Lambda = \left(\frac{\beta h^2}{2\pi m}\right)^{1/2}.$$  

(C.2)

Note that in this equation $m$ is the mass of a colloid and not the number of particles in the cluster, as is the case in chapter 4.

The quantities $Z_t$, $Z_r$ and $Z_v$ are independent of each other to a good approximation for the simulations of isolated clusters. This statement is equivalent to saying that there is only a weak coupling between the translational, rotational and vibrational degrees of freedom of the cluster.

At thermal equilibrium the relative frequency that a cluster is found in either the 6A or 6Z state is the ratio of the contributions of each state to the partition function. Therefore we must calculate $Z_t^{6A/6Z}$, $Z_r^{6A/6Z}$ and $Z_v^{6A/6Z}$ to find the relative frequency of the two states.
C.1.1. Translational contribution

The translational contribution \( Z_t \) is proportional to the volume of the system explored by the micro states characterizing each cluster type. In the simulations there are no boundaries and both 6A and 6Z clusters are able to explore the entire volume of the system. Therefore \( Z_t^{6A} \) and \( Z_t^{6Z} \) are identical.

C.1.2. Rotational contribution

The rotational contributions to the partition function are assumed to depend on the point group symmetry and the radius of gyration \( R_G \) of the \( T = 0 \) ground state configuration for each state.

\[
Z_t^{6A/6Z} \propto \frac{N \sqrt{mR_G}}{s}.
\]  
(C.3)

Again here \( m \) is the mass of each colloid. The numerator is the square root of the moment of inertia of the cluster about the mean position of the particles in the \( T = 0 \) ground state configuration.

The quantity \( s \) is the symmetry number of the cluster. It counts the number of ways that the cluster can be rotated around to yield arrangements that are indistinguishable from each other\(^1\).

The constant of proportionality relating \( Z_t^{6A/6Z} \) to the radius of gyration and the symmetry number depends only thermal and fundamental numbers. As it does not depend on the state (6A or 6Z) of the system it does not affect the relative frequency that each state is seen.

C.1.3. Vibrational contribution

Vibrations of the particles around their positions in the \( T = 0 \) equilibrium configuration must also be accounted for in the partition function. The vibrations are assumed to be approximately harmonic so that the contributions to the partition function can be calculated using the known result for the classical one dimensional harmonic oscillator.

The potential energy surface is expanded about the equilibrium configuration \( r_{GS}^N \) using a Taylor series as:

\[
U(r_{GS}^N + \delta r) = U(r_{GS}^N) + \delta r^T \nabla U(r_{GS}^N) \delta r + O(\delta r^3).
\]  
(C.4)

Note that the linear term in the Taylor series is not needed as the force is zero in the ground state configuration.

\(^1\)It is possible to distinguish between the rotated states if the particles are uniquely labeled. However the topological cluster classification (TCC) does not distinguish between these states, so the contribution of the symmetry number to the partition function must be included.
For small vibrations, the dominant vibrational correction to the energy of the ground state is from the quadratic term in the right hand side of equation C.4. A harmonic approximation is invoked to calculate the vibrational contribution to the partition function. The quantity $\nabla \nabla U(r_{GS}^N)$ is the Hessian matrix and its eigenvalues and eigenvectors describe the modes of oscillation of the cluster.

The vibrational contribution to the partition function for the classical one dimensional harmonic oscillator moving in the direction of one of the eigenvectors with eigenvalue $q_i$ is proportional to

$$Z_{v,i}^{6A/6Z} \propto \sqrt{\frac{2\pi}{q_i}}.$$  

(C.5)

As the eigenvectors are orthogonal, the total vibrational contribution is just the product of the contributions from each of the non-zero eigenvalues:

$$Z_v^{6A/6Z} \propto \prod_{i=1}^{3N-6} \sqrt{\frac{2\pi}{q_i}}.$$  

(C.6)

There are six zero-valued eigenvectors, corresponding to translations and rotations of the cluster in three dimensions.

### C.2. Relative frequency of 6Z to 6A

The quantities needed to calculate $Z_{6Z}/Z_{6A}$ are therefore $R_G$, $s$ and the eigenvalues of the Hessian for each cluster. We find $R_{6Z}^{6A}/R_G^{6A} = 1.06$, $s_{6A}/s_{6Z} = 12$ and $\prod \sqrt{q_i^{6A}}/\prod \sqrt{q_i^{6Z}} = 1.79$. Therefore $Z_{6Z}/Z_{6A} = 22.7$ is the frequency of 6Z clusters relative to 6A clusters.
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