LAW DISORDER

THE UNUSUAL CASE
OF WEAK COLLOIDAL
SOLIDS **Ruben Frederik Higler**

PROPOSITIONS

1. The enigma of the liquid state and its glass transition is best resolved by treating the liquid as if it were a solid.
(this thesis)
2. Strong glass transitions do not exist for repulsive isotropic spherical colloids.
(this thesis)
3. The beauty of the physical sciences does not lie in breathtaking nightly skies, it is not found in the bewilderment of the very small—
it is found in ideas that bridge distances and connect the world.
4. In the description of solids, the regular crystal is but an outlier while the disordered anti-crystal is closer to the norm.
(C.P. Goodrich et al., *Nat. Phys* (2014))
5. If John von Neumann and Alan Turing are the parents of digital computing; surely, its great-grandfather can only be Gottfried Wilhelm Leibnitz
("Explication de l'arithmétique binaire", *Mémoires de mathématique et de physique de l'Académie royale des sciences* (1703))
6. Cryptocurrencies combine everything we don't understand about the financial world with everything we don't understand about computing.
7. Complicated solutions for complex problems emerge when clear-thinking is left stranded.

Propositions belonging to the thesis entitled:

LAW & DISORDER
THE UNUSUAL CASE OF WEAK COLLOIDAL SOLIDS

Ruben Frederik Higler
Wageningen, 6 July 2018

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COLLOIDAL SOLIDS

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INTRODUCTION

1

States of Matter

ALL MATTER surrounding us is present in a physical aggregation state, or phase. We broadly recognise three different states: the gases, liquids, and solids (Fig. 1.1). Interaction with these three main phases is part of our daily lives. We are most familiar with the states of water, H_2O ; while cooking or preparing food we bring water from its liquid state into the gas state by heating. We can also go in the opposite direction and bring liquid water into its solid state by lowering the temperature, freezing. While water and its properties dominate our lives and all life on earth, it is by no means unique, as all matter can be found in one of these states. It should therefore not come as a surprise that the study of the different forms of matter and the transition between them form one of the central themes in physics research.

Over the centuries, scientific pursuit has given us highly accurate descriptions of, and predictions for the characteristics of the gas and solid state. By contrast, the liquid state is an enigma; it is a missing-link between the well-described gas and solid states. To explain the reason for this apparent lack of understanding it is best to start with liquids and solids.

Gases

Gases form by far the simplest aggregation state to understand. In a gas all constituent particles, atoms, molecules, etc., are separated by large distances. The particle motion is ballistic until they occasionally meet and collide. There is no maximum to the volume a gas can fill; give a gas more available volume and it will fill it. The investigation into the

Figure 1.1 – Three aggregation states of water: **(left)** Gas in the form of steam erupting from a geyser. Though what is actually visible are small condensed droplets of liquid water as gaseous water is invisible. **(centre)** Liquid in the form of the ocean covering most of the surface of our planet. **(right)** Solid in the form of ice blocks on an Icelandic beach. In fact, this image of a block of ice contains all three aggregation states of water.

'Steam Phase eruption of Castle geyser with double rainbow' by Broken Imagery is licensed under CC-BY-SA 3.0; 'Boat in storm at sea' by Angell Bob, U.S. Fish and Wildlife Service is in the public domain; 'Ice block at beach near Jökulsárlón, Iceland' by Andreas Tille is licensed under CC-BY-SA 4.0

thermodynamical behaviour of gases started at a time when the molecular model of the world was not generally accepted and as such the first empirical descriptions of gases are not based around this idea. The ideal gas law, in a form which we might recognise was first introduced in 1834 by Émile Clapeyron. He deduced the following relation: $PV = CT$, with C as a proportionality constant [1]. He arrived at his equation by combining Boyle's law, $P \propto V^{-1}$, which related the pressure of a gas to the volume it occupies, with the Gay-Lussac law, which states that there is a linear relationship between the pressure and temperature of a gas: $P \propto T$. While the gas law by Clapeyron proved highly successful, it was still based on the combination of two empirical laws. Only after the introduction of the kinetic theory of gases, which treats gases as statistical ensembles of moving and colliding particles, was there a way to arrive at the gas law from first principles. The derivation from the kinetic theory of gases — given that the average kinetic energy follows from the equipartition theorem as: $\langle E_{kin} \rangle = \frac{3}{2}k_B T$ — gives the ideal gas law we are all familiar with: $PV = nRT$, where P is the pressure, V the volume, and n the amount, in moles, of the gas. R is the ideal gas constant and T the temperature of the gas in K . As it turned out, the proportionality constant introduced by Clapeyron was the product of the amount of gas particles present and the ideal gas constant: $C = nR$. The specific chemical make-up of the ideal gas under study does not play a role here; it is the free motion of the particles and the lack of significant interactions between them which are important and govern the global behaviour of the gas. A such a gas has no regular structure what so ever; all particles

continuously and freely explore all volume available. The descriptions of gases described here, have been and still are very successful in predicting and describing the behaviour of gases.

Crystalline Solids

The free movement in gases is completely lost in solids. Whereas in a gas the particles are free to explore the entirety of the space available to them, in a solid they are confined to specific positions around which they vibrate powered by their thermal energy.

The most familiar solid structure is that of a crystal. In a crystalline structure the particles making up the solid, be that atoms, molecules, or colloids, all have a well defined equilibrium position around which they vibrate. Not only do individual particles have a well defined position, their position with respect to one another is also regular; all particles are located on a lattice which repeats in space. The smallest repeating unit of this regular lattice is called the unit cell (Fig. 1.2). The positions in a crystal have both long-ranged translational order — if we ‘pick up’ the lattice at some location, move it an integer number of unit cells and drop it, the new configuration will be indistinguishable from the previous — as well as rotational order — under certain rotation operations the resulting crystal is again indistinguishable from the start configuration. The rotational symmetries allowed for crystals are limited to 1, 2, 4, and 6 fold symmetries; these are the only rotations compatible with the requirement of long-ranged translational order.

In three-dimensional crystals there is a large collection of possible unit cells. In this thesis we will come across two of them: body-centred cubic (bcc) and face-centred cubic (fcc). In both cases the unit cell is a cube with a particle on each corner, but they differ in the placement of the remaining particles. In the case of bcc there is a single particle in the centre of the cube, while for a fcc unit cell there is one particle on every face of the unit cell cube (Fig. 1.3). The regular nature of crystals results in a diffraction pattern with well defined Bragg peaks. For a bcc crystal we show such a pattern in figure 1.4, left column. The pattern of peaks has, similar to the crystal, long-ranged translational and rotational order.

In a solid, the interactions between the particles play a important role. The result is a rigid state of matter with a finite volume at all temperatures which resists flow; it possesses a shear modulus higher than zero, $G > 0$ [2]. This fact forms the basic discrimination between solids and gases or liquids: while the latter two states flow freely, the solid resists any changes to its shape. All such actions will cost a finite amount of energy.

Thermodynamical descriptions of the behaviour of crystalline solids started in the 19th century. Similarly to the first descriptions of gases, the early observations were empirical in nature. In 1819 Petit and Du-

Figure 1.2 – Toy example of a crystal made out of banana-particles. The particles are arranged in a regular pattern which repeats in space. The unit cell of this lattice is indicated by the black solid rhombus.

Figure 1.3 – (top) body-centred cubic (bcc) unit cell. (bottom) face-centred cubic (fcc) unit cell.

long published their findings on the relation between the atomic mass of elements, M , and the specific heat capacity, c , of the pure solid form of the element. For a wide range of metals they found that the product of those two properties was approximately constant, $M \cdot c = K$, with the proportionality constant, $K \approx 24$ [3]. We would now recognise K to be equal to $3 \cdot R$, where R is the ideal gas constant.

Figure 1.4 – Three different structures found in solids. **(left column)** A crystal with long-ranged translational and orientational ordering; in this case an experimental colloidal bcc crystal. The corresponding diffraction pattern has been calculated directly from particle positions for the $[011]$ direction through the bcc crystal. Used with permission from [4] **(right column)** A quasicrystal with only orientational ordering; in this case a high-resolution transmission electron microscopy image of the real space structure of $\text{Al}_{63}\text{Cu}_{24}\text{Fe}_{13}$, found in the Khatyrka meteorite. The corresponding diffraction patterns clearly shows the ten-fold rotation symmetry of the quasicrystal. Used with permission from [5].

While the Petit–Dulong law holds for many elements in their solid aggregation state, numerous examples can be found which do not conform to this description; for example: carbon and silicon. This includes all molecules containing those elements. Since carbon forms the backbone of life and silicon came to dominate our digital technology, a better model was needed. The next breakthrough was made by Einstein in 1907. He used the ansatz that the particles on the lattice were undergoing continuous vibrations. With this idea he proposed a statistical description of solids as a collection of independent quantum harmonic oscillators on lattice sites [6]. He used the — at the time new — ideas of energy quantification in an harmonic oscillator to arrive at an approximate description

of solids for the first time. His description found the necessary temperature dependence of the specific heat as observed in experiments and at high temperature converged to the empirical Petit–Dulong law.

Einstein's description was a seminal piece of work. However, it was not complete; his description was incorrect in the low temperature limit. Debye used the way of thinking of Einstein — that of quantum oscillators — and extended it by not simply considering a solid as separate non-correlated oscillators but by only considering collective vibrations of the lattice, phonons. However, unlike photons, the available wavelengths for phonons are limited by the finite size of the solid and the finite minimal distance between neighbouring particles. From the allowed phonons and the number of degrees of freedom — $3N$: each particle supports one longitudinal and two transverse vibrations — in the system, Debye's model successfully predicted solid properties at low temperatures, the regime where Einstein's description broke down [7]. Just like the prediction by Einstein, Debye's model of a solid recovers the Petit–Dulong law at high temperatures.

Both of these models of solids do not take the specific interactions between particles, nor the microscopic structure of the solid into account. Intuitively it makes sense that the interactions and the structure do in fact matter. It was Max Born in 1939 who came up with a complete theory of solids which took both interactions and crystal structure into account [2, 8]. Born considered a solid as a microscopic central force network and he managed to connect his microscopic lattice theory to the familiar macroscopic elastic theories, thereby effectively closing the circle. Just as the descriptions of gases have the theories of the crystalline solid state been highly successful in describing the behaviour of this aggregation state.

While the solid state may appear well understood it is far from simple. In fact, while it is easy to classify a system as a solid, the underlying structure of the system can take many shapes. We have already discussed the idea of a crystal: solids which have a structure with long-ranged translational and long-ranged orientational order. However, this is not the only microscopic structure a solid can have.

There exists another class of crystalline solids where the strict requirement of long-ranged translational order no longer holds; these crystals are called quasicrystals. Dan Shechtman was awarded the 2011 Nobel prize in chemistry for their discovery [9]. Quasicrystals let go of the strict long-range translational order but keep orientational order; as such they can have all symmetries forbidden in crystals. Quasicrystals have been found with 5, 10, and 12 fold orientational symmetries [10, 11]. So far, only a few thermodynamically stable quasicrystals have been found [12, 13, 14, 15], including one in a meteorite [5] (Fig. 1.4 middle column). All these examples are metals with multiple atom species. Quasicrystals in three dimensions formed from simple monodisperse spheres exists so

far only in simulations and models [16, 17].

Liquids

In contrast with gases and solids there is no complete theory for the liquid state. In gases, particles are largely non-interacting and follow ballistic paths. In solids they only undergo local vibrational motion and have strong interactions. Liquids have no unique mode of motion. In the liquid, particles undergo a combination of vibrations around their positions and diffusive motion due to ballistic motion in between collisions. In liquids particles interact as the liquid is cohesive, but constantly swap their interaction partners. To complicate matters, the ratio between these two basic modes of liquid motion changes with temperature. If a liquid is close to its evaporation point, the dynamics will tend more towards the ballistic motion of gases, while close to the melting point they will more resemble solids [18]. Recent work on liquid theory has provided a new avenue of exploration to tackle the problem [19, 20]. Their approach is based on an idea of Y. Frenkel as set out in his monograph titled ‘A kinetic theory of liquids’ [21]. In the ideas of Frenkel, liquid particles vibrate around an equilibrium position until the particles jump to a different equilibrium position, a process activated by the influence of surrounding particles. These changes in dynamical modes are separated by an average time-scale, τ , the liquid relaxation time. This relaxation time-scale, τ , separates the solid-like and gas-like dynamical properties of the liquid phase. Whenever we are in a time regime which is faster than the liquid relaxation time the liquid is in fact capable of supporting both longitudinal and transverse vibrational modes; just as solids do [21, 22, 23, 24]. At these short time-scales the liquid thus behaves as a solid. The recent work on this *duality* of liquids shows that the thermodynamical properties of real-life liquids are dominated by the vibrational energy modes; their solid like properties dominate and effectively determine the thermodynamical properties of liquids [18, 25].

Amorphous Solids

It is possible for a liquid to gain such a high density that its liquid relaxation time increases by many orders of magnitude. The resulting phase behaves to all intents and purposes as a solid; this is in line with Frenkel’s idea of liquids behaving as solids below their liquid relaxation time. While this phase has the mechanics of a solid, it is structurally indistinguishable from liquids. There is only short-ranged order, reminiscent of liquids, but no long-ranged translational nor long-ranged orientational order as we find in crystals (Fig. 1.5). However, its dynamical behaviour is completely solid-like; they resist flow just as solids do [26, 2]. As such it

Figure 1.5 – (left) Computer rendering of an experimental binary colloidal glass without any orientational or translational ordering. The lack of order is reflected in the diffraction patterns (right), calculated from particle positions, by the presence of concentric Debye–Scherrer rings.

forms a third structural phase of a solid that just like quasicrystals loses translational order, but also has no orientational ordering. We call this amorphous solid a glass. The study of glasses and the transitions from liquids to glasses, crystals to glasses, and glasses to crystals form an extensive field of research. The research in this field focuses on trying to answer the question: How do microscopic changes lead to the dynamical arrest on a global scale?

Disorder in weak crystals

The structural disorder of glasses is not the only form of disorder present in certain solids. The dynamical behaviour of a system can also be a source for disorder. The fcc crystal is the densest packing of spheres [27] and maximises the number of nearest neighbours, with a coordination number $Z = 12$. Face-centred cubic crystals are therefore, from an enthalpic point of view, the most stable crystal configuration for systems where interactions take place on a short range between the first and second neighbours only [2]. However many elements and metals have a body-centred cubic structure. Especially at high temperatures near the melting point do many elements form bcc crystals. At these conditions the entropic contribution of the much more floppy bcc structure starts to dominate, $S_{bcc} > S_{fcc}$, and stabilises the bcc crystal [28, 29, 30, 31]. These high-temperature bcc structures are found for practically every metal in group one to six of the periodic table and for most lanthanides and actinides [32, 30]. In fact, in a seminal paper Alexander & McTague argue that all crystals should have bcc symmetry prior to melting as this is the most compatible with the liquid state [28].

Body-centred cubic crystals undergo substantial thermal fluctuations as a result of their entropic stability. These fluctuations occur especially

Figure 1.6 – Structural differences between an instantaneous snapshot of particle positions versus time averaged positions in a system of strongly repulsive disks. **(A)** Snapshot of particle positions coloured according to the value of the bond-orientational order parameter, ψ_6 , which we calculate according to: $\psi_6 = \left\langle \frac{1}{N_b} \sum_{i=1}^{N_b} \exp [6i\theta_{ij}] \right\rangle$. This parameter is unity for a perfect hexagonal packing and goes towards zero when disorder is introduced. **(B)** Averaged particle positions. The colour coding is the same as in **A**.

at high temperatures. As a result, bcc crystals close to melting exhibit anomalous behaviour. For example, the first-order solid-liquid transition becomes only marginally first order with a small amount of latent heat [4]. This behaviour is the result of nonaffine motions of particles which become important for systems with such large thermal fluctuations. In fact, while on average the system forms a perfect bcc crystal, instantaneous snapshots of the structure will show large deviations due to correlated heterogeneous dynamics (Fig. 1.6). In this respect weak crystals are an interesting subject of study as they exhibit different structures, either amorphous or crystalline, based on the frequency of interest. They in fact also show a *duality* in their behaviour.

Colloidal as big Atoms

The most fine-grained level of information we can acquire during experiments is information on the positions and movements of the smallest constituent particles present in the system. In the case of atoms or molecules this poses a severe challenge. The length and time scales involved in molecular processes are very small; a typical atom has a diameter on the order of 100 pm. Visualisation of materials at the atomic level is therefore very challenging. Often we can make a compromise and gain structural resolution by giving up on time resolution. For example, techniques like atomic force microscopy (AFM), scanning tunnelling microscopy (STM), or transmission electron microscopy (TEM) have all been used to image at a single atom [33, 34, 35, 36] or even single bond level [37]. However, if we want to study dynamical processes the trade in time resolution to gain structural resolution is of no use. Whenever scientists are presented with such a problem an obvious next step is to

Figure 1.7 – The experimental method of Jean Perrin. **(left)** Microscope chamber chambers as constructed by Jean Perrin. We still use the same construction as he pioneered. **(centre)** Microscopic photograph of colloidal emulsion droplets (black dots) in water. **(right)** The result of his particle tracking algorithm; the black dots represent the time points at which photographs were taken. The solid lines connect the particle locations through time to give particle tracks. All panels are reproduced from [40].

find a model system which can be studied on time and length scales which are easily accessible.

For such a model system we have to go to the colloidal world. At the colloidal length scales, 10s of nanometers to 10 micrometers, particles appear to behave in ways highly similar to their atomic counterparts. For example, colloidal spheres show the same crystallisation behaviour as atoms and molecules [38, 39], with the major difference that the controlling parameter in the atomic world is temperature, T , which in the colloidal world becomes the volume fraction ϕ .

The idea of using colloidal particles as a model system goes back to the early 20th century. Around this time Einstein was interested in the random motion of colloidal particles which had been observed by Brown; the so-called Brownian motion. He postulated that the random motion observed was the result of molecules from the solvent continuously bouncing against the colloids [41]. At the time the theory of molecules was not as accepted or experimentally tested as it is today. Einstein made predictions about the density distribution of particles as a function of height under the influence of gravity, the sedimentation equilibrium [42]. This prediction was experimentally tested by Jean Perrin with the use of colloidal particles [40]. With his experiments Perrin showed that the structure of matter was indeed discontinuous, in agreement with the molecular theory. The work received the Nobel prize in 1926 and brought the world of colloids to the attention of physical science.

In his experiments Jean Perrin painstakingly followed the movements of single colloidal particles in time using microscopic photography and tracing paper (Fig. 1.7) [40]; this remains to this day one of the central techniques of colloidal research although our data recording devices and analysis methods have modernised. We can image colloidal

systems in three-dimensions and time using confocal microscopy; we extract the locations of particles, with sub-pixel resolution, over time using computer particle locating and tracking algorithms. With these modern techniques the concept of *colloids as big atoms* is truly within reach.

Colloidal particles are a macro- or supramolecular concept in that they consist either of one large molecule or of many molecules. As a consequence their interactions are dominated by the chemistry of their surface. Since this is all chemistry, it is relatively easy to tune the morphology of the colloids or their surface interactions to whatever you can imagine. The earliest colloidal experiments were done on colloids with very short ranged repulsive interactions and minimised Van de Waals attractions, which approximated hard-spheres [38]. The current repertoire of available colloids range from long-ranged repulsive spheres [43] to highly anisotropic and magnetically active cylinders [44] and from microgel particles [45] to DNA coated colloids with very specific interactions [46].

Inspired by the big role disorder plays in the dynamical behaviour of solids we arrived at the following mission statement for this thesis:

This thesis aims to use the ‘colloids as big atoms’ paradigm to elucidate how disorder breaks conventional rules assumed to hold for solids. We will focus on: (i) structural disorder in the case of colloidal glasses, (ii) the structural and dynamical disorder of weak crystals with interstitial dopants, and (iii) disorder both in the structure of the material and in the constituent particles themselves in the case of compressible microgel particles.

In the following sections we dive deeper into the topics that form the backbone of the chapters in this thesis.

Doped Materials

The image of perfect solid crystals as we have described above gives a very limited view on what is really going on inside materials in the real world. The notion of a ‘perfect’ crystal with all particles on the exact lattice sites prescribed to them by their lattice does not exist. In fact, most properties of crystalline materials are not determined by their ‘perfect’ structure but by the amount and types of defects in the system.

There exists a wide variety of possible defects in crystals, involving a single or many particles. Here we will focus on those defects which only involve a single particle, a point defect. The most prevalent point defect is the vacancy. As the name implies, a vacancy defect is a lattice site without

Figure 1.8 – Three examples of point defects in crystals. **(A)** A vacancy defect where one lattice site is missing a particle. **(B)** In substitutional defect where at one lattice site an original particle has been replaced by a foreign particle. **(C)** Interstitial defects, where foreign particles are introduced into the system that are small enough to fit in the interstitial space between base particles.

a particle (Fig. 1.8A). This type of defect occurs naturally in every crystal and has an equilibrium concentration, f , of [47, 48]:

$$f = N \cdot \exp(-\Delta E/k_B T), \quad (1.1)$$

here N is the total number of lattice sites in the system and ΔE is the net amount of energy required for the formation of a vacancy. This energy cost follows from the energy required to break the bonds of a single particle and the energy gained by placing that same particle on the surface of the crystal. This enthalpic contribution is joined by an increase in entropy; a perfect theoretical crystal has zero configurational entropy, the introduction of a vacancy increases the number of possible distinguishable configurations.

A vacancy defect is a type of native equilibrium defect. It occurs naturally without outside input and has a certain equilibrium concentration. While vacancies do influence material properties — they can act as nucleation sites for melting [49, 50] — they are not the most useful. Non-native defects are more interesting, as the introduction of foreign particles into the system, doping, can severely change its properties. The prototypical example is the strengthening of iron by addition of low concentration of carbon to form steel [51]. The introduction of a foreign particle into the system can occur via two types of point-defects: (i) the foreign particle replaces one of the particles on the lattice, a substitutional impurity (Fig. 1.8B) (ii) the foreign particle sits in between the lattice sites on an interstitial site, an interstitial impurity (Fig. 1.8C).

Both types of doping are heavily exploited in modern day engineering to tune material properties to our wishes. Especially in the semiconductor industry the doping of silicon to tune its conductive properties is important. The introduction of Arsenic (As) into silica can act as an electron donor. The As atom has five electrons in its outer shell; four electrons will form bonds with Si, leaving one free to dissociate and be excited into the conduction band at sufficient temperatures. A similar effect can

be achieved by doping Si with Boron (B). However in the case of B doping the charge carrier will be a hole; boron only has three electrons in its outer shell and will bind one from the host crystal, Si.

Whether the dopants behave as a substitutional impurity or as an interstitial impurity is based mainly on the relative size of the dopant with respect to the base crystal particles. As the interstitial space between lattice sites is limited, only smaller dopants will be able to fit in these sites. Dopants in atomic systems are often introduced by way of diffusion from a phase consisting of pure dopants in direct contact with a phase of the material that is to be doped; this process follows Fick's law:

$$\mathbf{J}_n = -D\nabla n, \quad (1.2)$$

leading to the following differential equation:

$$\frac{\partial n}{\partial t} = D\nabla^2 n \quad (1.3)$$

Here n is the concentration of dopants and D is the diffusion constant of the dopants. Assuming that the dopant concentration is low and that the crystal is fully regular, so that the dopants experience the same environment irrespective of where they are in the crystal, D follows:

$$D \propto \exp(-E_A/k_B T) \quad (1.4)$$

where E_A is the effective energy barrier height which needs to be crossed before every diffusion jump from one location to a neighbouring one. In crystals these locations are well defined interstitial sites; the empty off-lattice positions between the particles in the crystal.

The assumptions made regarding the diffusion coefficient — low dopant concentration and identical environment irrespective of location in the crystal — do not necessarily hold for real life solids. We have already seen that anomalous lattice dynamics start to play a major role in weak solids close to melting; this raises the question how dopant diffusion is altered by the weak base lattice.

Glass Transition

Of all aggregation states discussed so far the glass is without any doubt the strangest. A glass shares the isotropic structure associated with liquids while still being a solid and thus resisting flow. Glasses form a highly useful class of materials and have been so for a big part of human history [52, 53, 54]. Their uses range from drinking vessels[55] to optical-fibres and from high-tech materials such as metallic glasses [56] to food items[57].

Glasses do not appear spontaneously. To create a glass, a liquid needs to be cooled at such a rate that the transition into a crystalline state is avoided [58]. This is necessary because the glass phase is not an equilibrium phase; the crystal has the lowest free energy and is the preferred conformation of the solid. Upon rapid cooling of a liquid the liquid's viscosity rapidly increases by many orders of magnitude as the liquid molecules are pushed together (Fig. 1.9). At the same time the structure of the system does not differ significantly from the liquid state (Fig. 1.10); the glass state forms an amorphous solid. The increase in viscosity can take a number of shapes which classify the rate at which the viscosity increases. The viscosity increase can follow Arrhenius behaviour as: $\eta = \eta_0 \exp(-E/k_B T)$ where E is some activation energy, we call this a strong glass. However, in the majority of glasses the increase in viscosity is super-Arrhenius; the viscosity increases ever more rapidly, this kind of glass is called a fragile glass (Fig. 1.9)[59, 60, 61]. This finding implies that for fragile glass formers the activation energy has to be temperature dependant: $\eta = \eta_0 \exp(-E(T)/k_B T)$. The fragility of a glass transition is captured by the rate of increase in viscosity at T_g :

$$m = \left. \frac{d \log_{10}(\eta)}{d(T_g/T)} \right|_{T_g} \quad (1.5)$$

this parameter is known as the fragility index. In his paper Angell rationalised the difference between strong and fragile glass formers as a difference in the layout of the potential energy hyperplane. In the case of a fragile glass this landscape should have a high density of possible configurations, while for strong glasses the number should be much lower. The exact reason behind the different behaviours remains as of yet unproven.

The name 'glass transition' is perhaps a slight misnomer. The liquid slows down gradually and continuously as the temperature is lowered and structural changes associated with traditional phase transitions do not occur. In fact, the liquid-like structure and the exponential or super-exponential increase in viscosity are the hallmark features of a glass. As a

Figure 1.9 – Angell plot of the glass transition for various atomic and molecular systems. The logarithm of the viscosity is plotted as a function of temperature normalised by the glass transition temperature, T_g/T . Figure reproduced with permission from [59].

consequence it is very difficult to pinpoint the exact temperature at which the liquid transitions into a glass, T_g ; this point is often taken at the point where the system is frozen on timescales of $\sim 100\text{--}1000$ s, corresponding to $\eta \sim 10^{12}$ Pa s. At these timescales the system is for all intents and purposes frozen for experiments. The temperature at which the viscosity reaches these levels will differ between different materials. Therefore the viscosity is often plotted versus T/T_g , the 'Angell plot' (Fig. 1.9). Instead of viewing the glass transition as a single point, it might be more fruitful to see it as a global trajectory with a global slowdown of system dynamics as the result.

The glass aggregation state is not exclusive to atomic, molecular or polymeric systems. Colloidal systems can also undergo a glass transition [62]. Many of the features of molecular glasses are also present in colloidal glasses. Their viscosity also increases strongly [63, 64], although in the case of colloids the increase is measured against the viscosity of the suspending medium and as a general rule-of-thumb we consider the liquid to have transitioned into a glass when $\eta/\eta_{\text{medium}} \sim 10^5$. Colloidal glasses also have the second hallmark feature of glasses: the structure of the glass is indistinguishable from that of the liquid [65]. We can therefore

Figure 1.10 — The difference between the global structure of glasses and liquids are minimal. As is illustrated here with the radial distribution function, $g(r)$, for (left) liquid Selenium at 258 °C and (right) vitrified Selenium. Figures reproduced with permission from [67].

use colloids as a model glass former. The control parameter in the case of colloids is not temperature, as is used in the molecular world, but rather volume fraction ϕ , as an effective inverse temperature. As a consequence we need to use different methods to avoid the crystal phase. This is most often done by introducing a polydispersity of size into the system or taking it to its extreme and working with two differently sized but mixed particle populations. Especially size ratios between the two populations in the range of 0.7–0.8 are known to be efficient glass formers [66].

The main challenge in the study of glasses is finding the connection between the global dynamic arrest of the material and some microscopic physical process which can explain this effect for both strong and fragile glasses. If a microscopic theory can not make a prediction for both strong and fragile glasses that would imply that those two modes do not form part of a single transition phenomena, but are in fact manifestations of two different transitions and the idea of an universal glass transition is lost. For the rest of this section we will focus on colloidal model glasses.

Colloidal glass transition

The classical colloidal system to approximate hard spheres consists of poly(methyl methacrylate) (PMMA) particles suspended in a solvent mixture which matches the refractive index of PMMA as best as possible and has salts to screen any charges on the particle surfaces [68]. The matching of refractive index between particles and suspending medium has two distinct advantages: the van de Waals forces are minimised and it is easy to image the sample in three dimensions using confocal laser scanning microscopy. While this system is by no means a true hard-sphere, it is the closest experimental approximation around. Just like a hard sphere system it has a maximum volume fraction of $\phi = 0.74$ when all particles are arranged in a fcc crystal configuration. However, it is possible for the system to arrest into a glass phase at $\phi = 0.58$, which could theoretically reach $\phi = 0.64$ at random close packing.

Figure I.11 – (A) Computer render of an experimental dense liquid. The 10% most dynamic particles are rendered as large spheres with the rest as small spheres. It is clear that the dynamics are highly heterogeneous as the most dynamic particles in the system form clear clusters. (B) Self-intermediate scattering functions, $F_s(q, t)$, of vitrifying suspensions of PMMA colloids with increasing volume fractions from left to right. The two step decay indicative of dense liquids and glasses is clearly visible. The solid lines are stretched exponential fits to the α -relaxation part of the full curve. (C) Probability distribution of single particle displacement, $P(\Delta x)$. The non-Gaussian shape is clearly visible by comparing the experimental data (open circles) with the Gaussian fit (dashed line). The solid lines are exponential fits to the distribution. (D) Relaxation times, τ_α , for hard spheres from experiments (solid circles) and simulations (open triangles). The red dashed line is a power law fit corresponding to the prediction from mode coupling theory while the blue solid line is a fit to the empirical Vogel–Fulcher–Tammann description of the glass transition: $\tau_\alpha(\phi) = \tau_\infty \exp [A/(\phi_0 - \phi)^\delta]$. Panels A and C reproduced with permission from [69]. Panels B and D reproduced with permission from [70].

In dense colloidal liquids particles start to become surrounded by other particles that form an effective cage around the particle of interest. As the volume fraction increases the cage become ever more restricted until full dynamic arrest occurs. To probe the dynamics of a colloidal glass we have to quantify the movement of particles inside their cages and between cages. The parameter of choice is the self-intermediate scattering function:

$$F_s(q, t) = \left\langle \frac{1}{N} \sum_{j=1}^N \exp [i\mathbf{q} \cdot (\mathbf{r}_j(t) - \mathbf{r}_j(0))] \right\rangle \quad (1.6)$$

where N is the number of particles in the system. This function correlates the self-motion of a particle over a distance $2\pi/q$ as a function of lag time, t . This function is accessible both from single particle level experiments and scattering experiments. The resulting curves are characterised by a two stage decay for liquids on the way to vitrification. At short times there is β -decay which is associated with particles rattling inside their cages. At long times we find α -decay which we associate with particles breaking out of their cages and displacing a distance approximately equal to their own diameter (Fig. 1.11B & C). As the dense liquid fully vitrifies the α -relaxation mode disappears and $F_s(q, t)$ does not relax at all, indicating full dynamical arrest.

It is obvious by now that during the glass transition the system undergoes system-wide dynamical arrest. However, microscopic investigations have revealed a more complex scenario. The global slowdown is not matched one-by-one with the same arrest at a single particle level. It turns out that the dynamics in a system approaching its glass transition become strongly heterogeneous [69, 71, 72]; some regions of the system are far more dynamic compared to other regions (Fig. 1.11 A). This heterogeneous distribution of dynamics in a vitrifying system is one of the few universal characteristics of the glass transition.

So far we have only considered glasses made from particles approximating the theoretical hard sphere. The wide variety of colloids available with varying interactions and shapes allow for research into glasses made up of more exotic particles. For example, the introduction of an attractive element into the interaction potential between particles changes the glass transition and even introduces a region where the glass melts before it vitrifies again, the re-entrant melting regime [73]. Changes in particle morphology, going from isotropic spheres to anisotropic tetrahedrons, have different effects. There is still the characteristic two-stage relaxation process combined with appearance of heterogeneous dynamics. However, as the particles are no longer isotropic there occurs a decoupling between rotational and translational diffusive modes. In the case of tetrahedrons the rotational diffusion slows down faster than the translational diffusion [74]. This is the exact opposite of the situation with spheres, where the translational diffusion slows down before the rotational diffusion [75].

Mode coupling theory

Few microscopic models exist for the glass transition. The only theory based on first principles is mode coupling theory (MCT) and as such it forms the most principled description of the glass transition available to us today. Mode coupling theory is based around the idea of caging of particles by their immediate surrounding neighbours. It is the density fluctuations of those cages which form the backbone of the theory.

Its central equation is an equation of motion which describes the time evolution of the intermediate scattering function, $F(q, t)$, as [76]:

$$\frac{d^2 F(q, t)}{dt^2} + \frac{q^2 k_B T}{m S(q)} F(q, t) + \int_0^t M(q, t - \tau) \frac{dF(q, \tau)}{d\tau} d\tau = 0 \quad (1.7)$$

This equation — described as ‘mathematically rich’ — captures the dynamical evolution of the intermediate scattering function as a convolution of itself with a memory kernel. One of the major predictions from simple MCT theory for hard spheres is a divergence of α -relaxation times at a critical volume fraction ϕ_c :

$$\tau_\alpha \sim (\phi_c - \phi)^{-\gamma}, \quad (1.8)$$

here ϕ_c represents the ideal kinetic glass transition as predicted by mode coupling theory. The shape of $F(q, t)$ as predicted by MCT is the same as found in experiments, with two separate relaxation time-scales, β and α [77]. For the relaxation at longer times, α , $F(q, t)$ can be approximately described as $F(q, t) \sim \exp \left[- (t/\tau)^\beta \right]$: a stretched-exponential function.

However, this simple form of mode coupling theory is not without faults. In particular the prediction of the power-law divergence of the relaxation times at ϕ_c gives predictions for ϕ_c which are too low compared to experimentally found glass transitions. Where MCT predicts full kinetic arrest at $\phi_c \approx 0.57$ – 0.59 experiments have shown that samples are still ergodic at these volume fraction and true full arrest does not take place until higher ϕ (Fig. 1.11D) [70]. One of the reasons for this difference between theory and experimental findings lies with the MCT assumption that all particle movement is Gaussian up to ϕ_c . Many experiments and simulations have found this not to be the case; at longer times the single-particle displacements distributions start to significantly deviate from Gaussian and develop exponential tails (Fig. 1.11C).

In this section we have only discussed the simplest mode coupling theory. Many improvements of the theory have and are being made to minimise the discrepancies with experimental findings. The field is going forward with the aim of capturing the full collection of glass transition phenomena from first principles.

Elastic models — The shoving model

There is one further theoretical model of the glass transition we would like to discuss, as our own descriptive model of our experimental findings in chapter 4 is based on it — the shoving model. Dense liquids are akin to

solids which flow as we discussed before, based on Frenkels ideas; local flow events tend to be rare as most motion takes place in the form of vibrations. The energy barrier for these rare flow events has to be much larger than $k_B T$, since a dense liquid is viscous [78]. The model starts with the assumption that the relaxation time is the cumulative effect of many of these rare local rearrangement events inside the system. For each of these rearrangement events to take place some energy barrier, $\Delta E \gg k_B T$, has to be crossed:

$$\tau_\alpha = \tau_0 \cdot \exp \left(\frac{\Delta E(\phi)}{k_B T} \right) \quad (1.9)$$

For one flow event to take place, space has to be created locally to the event. A sphere of radius r around the future rearrangement event has to grow by Δr such that there is free volume available for the event to take place; the surrounding particles have to be shoved aside. The shoving model postulates that the energy required for this volume increase is shear energy and is related directly to the instantaneous shear modulus, G_∞ [79]. The average relaxation time then becomes:

$$\tau_\alpha = \tau_0 \cdot \exp \left(\frac{V_c G_\infty(\phi)}{k_B T} \right), \quad (1.10)$$

here $G_\infty(\phi)$ is the instantaneous shear modulus which increases with increasing volume fraction and V_c is the characteristic increase in volume associated with a rearrangement event. While the shoving model shows very good agreement with a wide range of substances in experiment [80], it lacks a microscopic interpretation in terms of particle-particle interaction forces.

Force Methods

The properties of materials depend fundamentally on interaction forces between the components which make up the material. Regardless of the sources of these interaction forces, whether it be long-ranged electrostatic interactions or simple contact forces in semi hard spheres, the accurate measurement of these forces is a priority. The various forms of disorder, which break perfect order, discussed in this introduction all introduce stresses to the system. The measurement of those stresses is essential in enabling us to further link disorder to the responses of materials at a single-particle level. It is not just disorder where forces start to become important, also in self-assembly processes is an understanding of the forces involved essential [83]. To these ends there is a need

Figure 1.12 – (A) Force chain network in a two-dimensional amorphous granular packing as visualised by stress sensitive disk. Reproduced with permission from [81] (B) Visualisation of the stress field surrounding a vacancy in a two-dimensional colloidal crystal by the SALSA method. The experimental SALSA result is compared with simulations and theory. Reproduced with permission from [82]

to develop new methods to measure the forces associated with material stresses in-situ and in real time.

If we take one step up in length-scales we end up in the world of granular matter, where thermal effects stop to play a role of importance. Granular materials range from piles of sand to piles of dice, with the common denominator that these are systems dominated by contact forces between constituent particles. Smart use of materials whose refractive index changes with applied stresses have enabled researchers to visualise the distribution and measure the magnitude of forces acting between granular particles [81]. Their findings show that not all particles play an equally important role in the transmission of stresses in amorphous packings; it is a small subset of particles which forms a stress bearing network, the force-chain network (Fig. 1.12A) [84, 85]. Analogous contact force networks have been predicted from theory and simulations in thermal hard sphere amorphous packings [86].

In the colloidal world there are methods to measure forces between particles but they either are indirect measurements, which measure the interaction potential between particles, or measurements that can not be done in the bulk and measure only between isolated particles. The first category consists of methods used to extract the pair interaction potentials from the static structure, $g(r)$, in dilute systems based on the idea that at densities approaching zero the interaction potential can be found as the natural logarithm of the radial distribution function: $\lim_{\rho \rightarrow 0} g(r) = \exp(-\beta u(r))$ [87]. The second category contains methods like colloidal probe atomic force microscopy (AFM) [88, 89] and optical tweezers [90]. Both methods can accurately measure pN forces between colloids, but require the colloids to be isolated and cannot be used in-situ. Recent new impressive methods have been developed which are able to measure stresses as a result of crystal defects on an almost single-particle level. However these are limited to colloidal systems and are not yet usable in biological systems (Fig. 1.12B) [82].

What is needed in this field are methods which can measure tiny

Figure 1.13 – Novel methods of measuring forces using single polymeric entropic springs can measure forces as small as 300 fN depending on the extension of the sensing polymer. The method is based on FRET, with FRET donors in green and FRET acceptors in red in the schematic computer rendering of the system. Reproduced with permission from [91]

forces, on a grey-scale, and preferably with a high flexibility in their usage; so that it can be adapted for use in many different systems. Such a measurement platform could be used to not only study forces between colloids but also between arbitrary components in biological systems. For example, as a means to measure forces involved in DNA replication, forces involved in the active transport of cell components, or those associated with crowding effects on enzyme folding. Recently one such system has been developed, which has the possibility to be adapted to each of these scenarios. The method is based on the usage of polymers with internal Forster resonance energy transfer (FRET) to create an ‘optical force spring’. The system was able to measure forces up to 300 fN in a single polymer spring (Fig. 1.13) [91]. It would be highly interesting to investigate other force measurement systems which use the ideas behind FRET in polymers to gain access to force-distance relationships.

Outline

This thesis explores how disorder, in the shape of structural disorder, dynamic disorder, or a combination of both, changes the behaviour of soft condensed materials

In chapter 2 we investigate how interstitial dopants behave in a weak crystal matrix that is close to melting. We find anomalously slow dynamics and the emergence of matrix mediated attractions between dopants. Both of these effects are due to the weak and dynamically disordered base crystal.

In chapter 3 we extend the work done in chapter 2 by focusing on the regime of large concentrations of dopants. We investigate the full extent to which the emergent attractive forces can lead to phase separation between dopants and base crystal. This chapter opens up the possibility

of experimentally studying solid-solid phase separations in weak solids in the future.

Chapter 4 shifts the focus from dynamical disorder to systems with both structural and dynamic disorder. We experimentally examine colloidal glasses made up of particles with very long ranged repulsive interactions. We apply the ideas of Frenkel and Trachenko and investigate the glass transition in our system from the perspective of dynamical force networks. Based on the shoving model we arrive at a quantitative description of the glass transition without fitting parameters.

Chapter 5 extends the analysis of chapter 4 with the aim of making our methods available for scattering experiments with the hope that the ideas behind dynamical connectivity transitions can be tested on a wider gamut of systems. With the aid of the Vineyard approximation we arrive at a method of extracting dynamical coordination numbers from data easily accessible by scattering methods.

In chapter 6 we experimentally study a highly asymmetric binary sized amorphous system. We develop the method of contrast variation multi-speckle diffusing wave spectroscopy with the aim of studying the decoupling of the glass transitions between both populations of particles. The system is not only amorphous in structure but is also comprised of microgel particles which can swell and deswell based on the osmotic pressure they experience.

Chapter 7 shifts the focus fully on the deswelling behaviour of amorphous packings of microgels. These highly deformable microgel glasses have been postulated to form the colloidal equivalent of molecular strong glass formers. We investigate these claims via Monte Carlo simulations and find that this is not the case; a case where colloids are not a perfect model system for the molecular world.

In the 8th and final chapter we start development towards a system for measuring and visualising contact forces in colloidal packings. The system we design is inspired by the polymer chain FRET force sensors. With our research we make the first steps towards our goals. Our findings inspired new design goals for the next generation of colloidal force sensors. While we get promising results we do not reach our goal completely. However, we open the way for future research to try and complete the project.

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ANOMALOUS DYNAMICS OF INTERSTITIAL DOPANTS IN WEAK CRYSTALS

2

The dynamics of interstitial dopants governs the properties of a wide variety of doped crystalline materials. To describe the hopping dynamics of such interstitial impurities, classical approaches often assume that dopant particles do not interact and travel through a static potential energy landscape. Here we show, using computer simulations, how these assumptions and the resulting predictions from classical Eyring-type theories break down in entropically-stabilised body-centred cubic (bcc) crystals due to the thermal excitations of the crystalline matrix. Deviations are particularly severe close to melting where the lattice becomes weak and dopant dynamics exhibit strongly localised and heterogeneous dynamics. We attribute these anomalies to the failure of both assumptions underlying the classical description: i) the instantaneous potential field experienced by dopants becomes largely disordered due to thermal fluctuations and ii) elastic interactions cause strong dopant–dopant interactions even at low doping fractions. These results illustrate how describing non-classical dopant dynamics requires taking the effective disordered potential energy landscape of strongly excited crystals and dopant–dopant interactions into account.

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Introduction

DOPING pure crystalline solids with small amounts of interstitial impurities is a widely used method to enhance material properties such as heat and electric conductivity [1, 2, 3, 4] or to tailor mechanical properties [5]. Prototypical examples include the introduction of carbon atoms in iron crystals to make steel or the doping of plastic crystals with Li-ions to create solid-state batteries [4]. To ensure longevity of doped materials, it is essential that the spatial homogeneity and transport dynamics of the dopants within the crystal are well controlled and understood. Although theories and models are abundant [6, 7, 8, 9, 10, 11, 5], it remains unclear how large thermal excitations of the matrix lattice affect the dynamics of dopants. This becomes of particular interest during the processing of doped crystals, where they are heated close to or beyond their melting point. For example in body-centred cubic (bcc) iron doped with carbon, significant deviations from the exponential increase of diffusivity with temperature, expected from Arrhenius' law, are observed close to the melting temperature where lattice excitations are strong [12].

While doping is typically performed to tailor material properties at the macroscopic scale, these enhanced properties emerge from the dynamics and interactions between dopants at scale of individual atoms [13]. In classical theories for dopant dynamics, impurity particles are described as hopping through a potential energy landscape which is set by a perfect lattice symmetry, with transition rates governed by the energy barriers between adjacent interstitial sites and their occupancy [14, 6, 7]. In reality, thermal fluctuations of atoms away from their equilibrium lattice positions will randomise the instantaneous potential energy landscape that the dopants experience; this could lead to failure of classical approaches to capture the physics of impurity diffusion when lattice excitations become pronounced. This may be particularly severe for crystals of the bcc symmetry, such as the high-temperature lattice of sodium, lithium and iron. In these high-temperature bcc phases, thermal fluctuations are large due to the relatively low coordination number; in fact, these fluctuations increase the entropy of the solid to such an extent that they are responsible for its thermodynamic stability [15].

For impurity transport in structurally-disordered colloidal glasses, it was recently shown that thermal fluctuations which create time variations in the potential energy landscape can have a strong effect on the dopant diffusivity [16, 17]; yet these effects remain largely unexplored for

very soft crystals which exhibit an on average ordered lattice.

In this chapter we study the dynamics of interstitial dopants in bcc crystals prepared from colloidal particles interacting by long-ranged electrostatic interactions. Using Brownian Dynamics simulations we probe in detail how strong thermal fluctuations of the base crystal affect the spatial homogeneity of the dopants and their motion through the lattice. Dopants within a static base crystal obey quantitative predictions of classical transition-state theory; by contrast, the same impurities diffusing in a fluctuating crystal exhibit completely different behaviour. We show how thermal excitation of the lattice causes clustering of the interstitials while simultaneously giving rise to strong disorder in the instantaneous potential energy landscape. This results in heterogeneous and anomalous dynamics of interstitials within an on-average perfect lattice. We support these observations with direct imaging experiments on a colloidal system using confocal microscopy. These data illustrate how large thermal fluctuations can give rise to heterogeneous dynamics in ordered solids, which cannot be captured by classical hopping theories.

Results

The classical approach to describe the diffusion of interstitial impurities through a crystalline matrix starts with the assumption that the dopants experience a static potential energy landscape set by the summation of interactions between a dopant and all particles in the base crystal [14]. If we assume that interactions between dopants are negligible, i.e. that the dopant concentration is low and the interstitial site occupancy approaches zero, this approach reduces to a simple transition-state theory for thermally-activated jumps between neighbouring minima in the energy landscape.

In a bcc crystal the minima in which interstitial impurities will reside are the tetrahedral sites (Fig. 2.1B, green spheres) [18]. We can identify two transition paths between tetrahedral sites that are most likely to contribute to the motion of a dopant. The first comprises the shortest path from one tetrahedral site to another (T–T transition) during which displacement the particle crosses a saddle point in the energy landscape. The second (T–O–T transition) goes from a tetrahedral site through an octahedral site to an adjacent tetrahedral site [18]. The rate at which these hops occur is governed by the energy barrier U_A separating two sites along either path.

We parametrise our simulations to match an experimental system of charged PMMA particles in an apolar solvent, which forms bcc crystals at

Figure 2.1 – (A) Schematic representation of a bcc unit cell. (B) The interstitial sites in a plane of the bcc unit cell with tetrahedral sites in green and octahedral sites in red. The T–T path (green) and T–O–T path (red) are indicated with lines connecting the interstitial sites. The potential field felt by the dopant is shown in the background. The values are the potential energy with respect to the global minimum at the tetrahedral site. Yellow indicates values of 20 $k_B T$ and above. (C) Hopping barrier $U_A(\phi)$ along a T–T (green circles) and T–O–T path (red squares) from numerical calculations. The solid lines are a parametric fit to $U_A(\phi)$ as described in the text, the dashed line indicates the melting point ϕ_m .

low densities [19, 20]. In these colloidal systems, the main control parameter is particle volume fraction ϕ . The crystals are formed from colloids with a diameter $\sigma_b = 1.8 \mu\text{m}$ and doped with interstitial impurities with $\sigma_d = 0.9 \mu\text{m}$. The interactions are described by Yukawa potentials to map the simulated phase behaviour as a function of ϕ onto that determined experimentally (see Fig. A2.1 in the Appendix and The Materials & Methods section of this chapter). For a perfect bcc lattice we can now compute the activation energy for both the T–T and T–O–T paths by summing the potential energy fields, taking long-ranged contributions into account. The bcc crystal exhibits a periodic network of energy minima (see Fig. S3), which provides an efficient means for interstitial motion on large length scales [18]. For the colloidal bcc crystal, the numerically enumerated transition energies are few to several $k_B T$ and the difference in activation energy between the T–T and T–O–T paths are small (symbols in Fig. 2.1C). To describe these data in a phenomenological way, we consider the difference between the summed potential field at the interstitial

site where U exhibits a minimum and the transition maximum

$$U_A(\phi) = U_+(\phi) - U_-(\phi) = \epsilon \left(\frac{e^{-\kappa g_+ a(\phi)}}{g_+ a(\phi)} - \frac{e^{-\kappa g_- a(\phi)}}{g_- a(\phi)} \right) \quad (2.1)$$

, where $a(\phi) = \left(\frac{\pi}{3\phi}\right)^{\frac{1}{3}}$ is the normalised lattice constant in units σ_b and the geometrical constants g_- and g_+ account for the potential energy fields at the minima and maxima, respectively. We use this empirical equation to fit the simulation data at discrete values of ϕ ; with values of $g_+ = 0.348$; $g_- = 0.345$ for the T-T transition and $g_+ = 0.297$; $g_- = 0.295$ for the T-O-T this relation describes our numerical calculation data well (lines Fig. 2.1C).

Within the classical approach, the rate at which transitions occur is governed by a thermally-activated process of the Eyring type:

$$k_h = k_{h,0} \exp(-U_A/k_B T) \quad (2.2)$$

The Brownian attempt frequency, $k_{h,0}$ is given by:

$$k_{h,0}(\phi) = D_0/d_h^2(\phi) = k_B T / (d_h^2(\phi) 6\pi\eta\sigma_d/2) \quad (2.3)$$

, in which d_h is the length of the transition path and D_0 is the self-diffusion coefficient of the interstitial impurities in a solvent of viscosity η . The long-time diffusion coefficient of the interstitial impurities as a function of volume fraction of the bcc crystal can now be predicted as

$$D_l(\phi) = d_h^2(\phi) k_h(\phi) = D_0 \exp(-(U_A(\phi)/k_B T)^\beta) \quad (2.4)$$

in which the stretch exponent β accounts for a distribution in hopping times due to the similar barriers of the two different transition paths.

To test the validity of this prediction based on classical transition state theory, we simulate the Brownian dynamics of interstitial impurities within a static and perfect bcc crystal (Fig. 2.2A). The potential energy field experienced by the dopants exhibits clear minima at the tetrahedral sites (crosses, bottom Fig. 2.2G). This leads to characteristic hopping dynamics in the trajectories of individual interstitial impurities, with particles vibrating within a tetrahedral site until they hop to a neighbouring site (Fig. 2.3A & C). Over time, the interstitial impurities probe the entire matrix by travelling through the interconnected network of local minima (see Fig. A2.3 in the Appendix). This gives rise to a mean-squared displacement $\langle \Delta r^2(\tau) \rangle$ as shown in the left panel of Fig. 2.4B); at short times vibrations within the interstitial sites give rise to subdiffusive motion. This transitions into diffusive behaviour at times longer than the Brownian self-diffusion time, $\tau \gg \tau_B$, as particles explore the lattice by

Figure 2.2 – Structural features of the bcc crystal for the simulation with a static (**A**, **D** and **G**) and dynamic base crystal (**B**, **E** and **H**) and the experiments (**C**, **F** and **I**). **A–C**: snapshots of bcc crystals at $\phi = 0.14$, in which particles are colour-coded according to their instantaneous bond-order parameter $\bar{q}_6$ and dopant particles rendered in orange (**A** & **B** only). **D–F**: Pair correlation functions $g(r)$. **G–I**: Potential energy landscape through four unit cells within the on-average ordered lattice, where black disks indicate the hard-sphere radius of the base crystal particles and the grey areas indicate the volume, from which the centre-of-mass of dopants is excluded, due to dopant-base particle overlap.

hopping between interstitial sites; this is characterised by a long-time diffusion coefficient D_l (circles in Fig. 2.4A & Fig. A2.5 in the Appendix). The simulation data for this static scenario are described very well by the prediction for $D_l(\phi)$ from transition-state theory, with $\beta = 0.61 \pm 0.01$ used as a fit parameter (line in Fig. 2.4A). The fact that β deviates from unity indicates a heterogeneous hopping process occurring both via the T–T and T–O–T transitions; the relative occurrence of T–T versus T–O–T hops is expected to be 3.5:1 based on the difference in activation energies taking into account the number of possible T–T and T–O–T transitions from a given tetrahedral site. We note that at this point, we have not established an exact and quantitative relationship between the value of β and the ratio of hops occurring via the two possible transition routes.

In real materials, at least one crucial assumption in this classical approach fails as the matrix in which dopants diffuse itself is also excited by thermal fluctuations. Especially for body-centred cubic crystals in close

proximity to their melting point, at which temperatures doped crystals are processed to induce ductility and malleability, these fluctuations are known to be strong [15]. Allowing the bcc phase in these colloidal systems to fluctuate retains an on-average perfect structure as evident from distinct Bragg peaks in their structure factor (see Fig. A2.2 in the Appendix). However, snapshots of the instantaneous structure show significant deviations from a perfect lattice as particles displace significantly from their equilibrium positions. Reconstructions of the system in which the particles are colour-coded according to their instantaneous bond order parameter $\bar{q}_6$ [21] illustrate the significant amount of thermal disorder within these bcc crystals, both in-silico and in experiments (Fig. 2.2B & C). The thermally-excited excursions of particles from their average lattice position translate into peak broadening in the pair-correlation function $g(r)$ (Fig. 2.2E & F). We note that $g(r)$ for experiment and simulation are in excellent agreement, even though the field-of-view in our measurements is limited due to experimental constraints. Even though the thermal disorder in these fluctuating bcc crystals is strong, it can still be structurally distinguished from a liquid by means of spherical harmonic bond-order parameters (see Fig. A2.4 in the Appendix), to probe local structure, and the existence of well-defined Bragg peaks in the structure factor (Fig. A2.2 in the Appendix) which signals the presence of long-ranged order.

The effect of the instantaneous deviations from a perfect lattice due to thermal excitations becomes apparent when we plot a snapshot of the potential energy landscape that a dopant particle experiences at a given time. Instead of the regular landscape that exhibits minima at tetrahedral interstitial sites, the fluctuating bcc crystal presents an apparently disordered potential energy landscape (Fig. 2.2H) in which the variations in the height of energy barriers and the depth of localisation wells are significantly larger as compared to the perfect lattice. Also from experimental data we can reconstruct the potential energy landscape; we obtain the particle positions from three-dimensional image stacks. Using the pair interaction potential obtained by inversion of pair correlation functions [22] and assuming that the interaction potential is pairwise additive, we can compute the potential energy of inserting a dopant particle at a given location within the lattice. Also the energy landscapes reconstructed in this way from snapshots of the experimental system, exhibit strong disorder (Fig. 2.2I).

This high degree of instantaneous disorder in the energy landscape results in very different interstitial dynamics than those predicted by the classical theory. The dopant particles are to a stronger degree localised, and transitions between minima appear at much lower frequency as compared to a static crystal (Fig. 2.3). As a consequence, the ensemble-averaged mean-square displacements exhibit a localisation plateau

Figure 2.3 – (A & B) Trajectory of a single interstitial dopant in the crystalline matrix over $\Delta t = 29 \tau_b$ in a static (A) and $\Delta t = 150 \tau_b$ in a dynamic bcc crystal (B). (C) interstitial displacement with respect to $t = 0$ in a static (bottom line) and dynamic base crystal (top line)

which extends by several orders of magnitude (right panel, Fig. 2.4B), resulting in a strongly reduced rate of diffusion at long times. To confirm that the interstitial mean-squared displacement converges to a diffusive behaviour at long times, we run a longer simulation up to $2 \cdot 10^4 \tau_B$. Indeed, the upturn we see in Fig. 2.4B becomes diffusive at even longer times (Fig. A2.5C in the Appendix).

We can extract D_I from these data by extrapolating the mean squared displacement to infinite time; see the Appendix for a detailed description of our method. Allowing the crystal that surrounds the interstitial impurities to fluctuate results in more than two orders-of-magnitude reduction in the diffusion rate (blue symbols Fig. 2.4A). Clearly, the effect of thermal excitations of the lattice cannot be ignored in describing dopant dynamics in bcc crystals.

Two possible contributions to this drastic reduction in interstitial diffusion rate can be identified. First, static or low-temperature bcc crystals feature a percolated path of T–T transitions, providing an efficient pathway for interstitial diffusion over large length scales [18]. The percolated path of transitions is the result of the centre-of-inversion symmetry of the bcc lattice. In the thermal bcc phase, especially close to melting, thermal excitations of the lattice are so pronounced that the *instantaneous* centre-of-inversion symmetry is lost. Note that this only applies to instantaneous snapshots of the structure, whereas time-averaging cancels out these fluctuations and restores the bcc symmetry, for example evidenced by the distinct Bragg peaks in the time-averaged structure factor (Fig. A2.2 in the Appendix). As thermal fluctuations break the local and instantaneous symmetry, the percolated transition path that relies on this symmetry is also lost. This is evidenced in the potential energy isosurfaces reconstructed from snapshots of the thermal bcc lattice in Fig. A2.3 (Appendix).

Figure 2.4 – **(A)** Long-time diffusion coefficients D_l as a function of distance to the melting point $\phi - \phi_m$ for static (circles) and dynamic crystals (triangles), with $\phi_m = 0.061$ as determined in the Appendix Fig. A2.1. Open symbols indicate D_l determined from the mean-squared displacements at $\tau = 5 \cdot 10^2 \tau_b$, while filled symbols are computed by extrapolating $\langle \Delta r^2 \rangle$ to infinity. Solid line is a fit to the transition-state prediction for $D_l(\phi)$, as described in the text. **(B)** $\langle \Delta r^2 \rangle$ for individual particles, with the ensemble-average $\langle \Delta r^2 \rangle$ (thick line) superposed for fixed (left) and dynamic crystal (right).

Secondly, as the potential energy landscape is strongly time-varying, hopping now requires not only a fluctuation large enough to escape a local minimum, but also the simultaneous availability of a low-energy pathway that remains open during the transition event. In effect, two competing frequencies come into play; i) that of escape attempts of the dopant and ii) the frequency with which the potential energy landscape reconfigures. As the Brownian time scales of the base crystal and the dopants do not differ by much due to the moderate size asymmetry, escape events now become cooperative and thus significantly less likely. It is known that the effect of fluctuating barriers on hopping is strongly non-monotonic and can lead to either enhancement, when the two frequencies become resonant, or reduction in transition rates [23, 24]. As we work in the classical limit, where the transition itself is not instantaneous but requires a finite time, this poses the additional constraint that the path remains open for the duration of the transition event, which further slows down hopping. The combination of these events leads to a strong quenching of the interstitial mobility in fluctuations bcc lattices.

A key feature for particles in disordered potential landscapes is the emergence of heterogeneous dynamics. To investigate this, we plot the time-averaged $\langle \Delta r^2 \rangle$ for all interstitial particles individually. For the

static crystal, no heterogeneities in particle dynamics are observed, with all mean-squared displacements collapsing onto the ensemble average (Fig. 2.4B left panel). By contrast, for the fluctuating bcc crystal, strongly heterogeneous dynamics are observed, with a large in-homogeneity in the single-particle behaviour (Fig. 2.4B right panel).

To explore the origins of these distinct heterogeneous dynamics within a on-average ordered solid, we reconstruct snapshots of the interstitial positions. While dopants are homogeneously distributed for the static crystal (Fig. 2.5A), they exhibit strong clustering in the fluctuating bcc over the entire range of base crystal densities ϕ (Fig. 2.5B and Fig. A2.7 in the Appendix). We hypothesise that this clustering is caused by the lattice strain accompanying the insertion of a single interstitial impurity into a tetrahedral site. Clustering between interstitials minimises the overall elastic deformation of the matrix and is thus energetically favourable. This gives rise to an emergent elastic attraction between the impurity particles. Similar lattice-strain mediated interactions are well-established to exist for crystallographic defects that cause a lattice deformation [25]. Indeed, we observe a strong increase in the lattice strain, defined as the average displacement of base crystal particles from their equilibrium position $\Delta r_{b,l}$ normalised to the lattice constant a , as a function of the distance to a nearest impurity.

We observe that the clusters are highly dynamic, with spontaneous particle association and dissociation (Fig. A2.6–A2.8 in the Appendix). This indicates a dynamic equilibrium between singlets (S) and bound states (B) $nS \rightleftharpoons B_n$, in which the association constant depends on the effective attractive potential U_{eff} emerging through the elasticity of the matrix: $k_a \propto \exp(U_{eff}/k_B T)$. We observe a significant fraction of singlets in stable coexistence with clusters, which does not evolve over time after equilibrating our simulation system (see Fig. A2.9 in the Appendix). This suggests that the effective attraction strength is of the order of the thermal energy $k_B T$; the dynamic equilibrium between clusters and singlets resulting from a balance between the configurational entropy of distributing impurities across the lattice and the enthalpic gain upon forming a cluster. This is further corroborated by the distribution of cluster sizes $P(S_C)$ (Fig. 2.5F). These data are well described by an exponential decay as indicated by the solid line in Fig. 2.5F. This indicates that clusters are formed by an open association process governed by a dynamic reaction equilibrium between unimeric dopants and clusters.

In this chapter we demonstrated how thermal fluctuations can lead to the failure of classical theories for dopant dynamics and give rise to complex, heterogeneous, and anomalous dynamics in an on average ordered matrix. Large instantaneous deviations from a perfect lattice due to thermal excitations cause a disordered potential energy landscape in which interstitial atom diffusion can be orders of magnitude slower

Figure 2.5 – **(A & B)**: Dopant positions in a snapshot at $\phi = 0.07$, in which particles belonging to the same cluster are colour-matched, while singlets are displayed in grey for static (A) and dynamic base crystals (B). **(C & D)** Particle trajectories of all particles over a time interval of $2 \cdot 10^{-3} \tau_b$ for static (C) and dynamic (D) base crystal. **(E)** Lattice strain $\Delta r_{b,l}/a$, taken as the average deviation of particle positions with respect to their equilibrium site, as a function of distance to a dopant for $\phi = 0.07$ (circles) and 0.12 (squares). **(F)** Distribution of cluster sizes $P(S_C)$ for $\phi = 0.07$, fitted with an exponential distribution $P(S_C) \propto e^{-S_C/S_C^*}$ with $S_C^* = 0.96$ the characteristic cluster size (red line).

than expected based on transition state theory. Our simulations also give rise to a microscopic picture of the strongly heterogeneous dynamics of interstitial dopants: elastic interactions between dopants cause them to agglomerate within the lattice, which in turn locally softens the matrix and gives rise to enhanced mobility. The coupling between spatial organisation of the dopants, the local properties of the matrix and resulting dopant dynamics can be expected to play a crucial role in the effective tailoring of material properties using doping. Arriving at a complete description of these complex dynamics would require extension of classical lattice dynamics to account for both the fluctuating and locally disordered energy landscapes, for which a framework was developed for glasses [24], and for the emergent interactions and spatial inhomogeneity of the dopants.

Materials & Methods

Simulations

We perform Brownian Dynamics simulations using HOOMD-BLUE, a GPU accelerated software package, in single-precision mode [26, 27]. Analysis routines are all written in the python programming language, using scipy, numpy, lmfit, scikit-learn, matplotlib, and mayavi [28, 29, 30, 31, 32, 33] libraries. For the calculation of bond order parameters we use BondOrderAnalysis [21] and we calculate Voronoi cells using the voro++ package [34]. All quantities are expressed in normalised units, in terms of base particle diameter σ_b , base particle self-diffusion time τ_b and $k_B T$ respectively.

Simulations are performed in the canonical ensemble (or N,V,T-system) with periodic boundaries. Systems consist of two types of particles, one that forms the crystalline matrix ($\sigma_b = 1.8 \mu\text{m}$) and the dopants ($\sigma_d = 0.9 \mu\text{m}$). This size ratio of 0.5 is experimentally accessible and close to that for carbon-doped iron and lithium-impurities in silicon [35]. The particles interact via Yukawa potentials parameterised using experimental data (see below). The simulations assume pairwise additivity of the potentials; in the experimental system of charged colloids many-body effects are known to occur [36]. Nonetheless, in previous work we have established that pairwise additive BD simulations can capture the main behaviour of experimental crystals of the charged colloids we simulate here [37].

Brownian Dynamics integration, using the overdamped Langevin equations, are performed with a time step of $2.5 \cdot 10^{-5} \tau_b$, in one of two ways, either both particle types are integrated for the dynamic crystal or only the dopant particles are subjected to integration for the static matrix. In all cases we simulate $N = 13718$ base crystal particles. Dopant particles are placed randomly at tetrahedral interstitial sites in the pristine bcc lattice in a ratio of 1:47. Simulations are run for at least $2 \cdot 10^3 \tau_b$, preceded by an equilibration time of $2 \cdot 10^2 \tau_b$.

Experiments

Some aspects of the simulation results are experimentally verified by studying a system of polymethyl methacrylate particles, stabilised by polyhydroxystearic acid.[20] Particles with diameters of $\sigma_b = 1.8 \mu\text{m}$ and $\sigma_d = 0.9 \mu\text{m}$ are prepared using established procedures [38]. We suspend the particles in a density matching solvent mixture of *cis*-decalin and tetrachloroethylene, in which 10 mM Aerosol OT is added to charge the

particles [20]. We image the samples in three-dimensions and time using confocal fluorescence microscopy using a VisiTech Infinity-3, mounted on a Nikon Ti-U and equipped with a Hamamatsu ORCA-Flash 4.0 camera. Three-dimensional volumes of $50 \times 50 \times 30 \mu\text{m}^3$ are acquired at 1Hz. Particle centroid positions are determined and linked together in time using well established methods based on the fitting of a Gaussian curve [39].

Mapping

The particles in the simulation interact via the Yukawa potential:

$$U(r)/k_B T = \epsilon \frac{\exp(-\kappa\sigma(\frac{r}{\sigma} - 1))}{r/\sigma}$$

. In the solvent we use, the inverse screening length κ is determined to be $1.8/\sigma_b$ [20]. To define the interaction strength ϵ we map the simulation data onto the experimentally-determined melting point of the bcc crystal (Fig. S1). An $\epsilon_{b,b}$ of 713 gives a melting point at a volume fraction ϕ of 0.061 *in silico* close to the melting point found experimentally, $\phi = 0.060$. For the smaller dopants we assume a particle-size independent surface charge density such that $\epsilon_{d,d} = 227$. The cross interactions between dopant and matrix is taken as the average of the base-base interaction and the dopant-dopant interaction ($\epsilon_{b,d} = 470$). Data analysis methods are described in the appendix.

Appendix

Determination of the phase diagram

To accurately define the melting point ϕ_m and the region where liquid and bcc crystal coexist, we calculate, for every particle, the averaged bond order parameter following the approach described in [21]:

$$\bar{q}_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l |\bar{q}_{lm}(i)|^2} \quad (2.5)$$

for $l = 6$ or $l = 4$ and where

$$\bar{q}_{lm} = \frac{1}{\widetilde{N}_b(i)} \sum_{k=0}^{\widetilde{N}_b(i)} q_{lm}(k) \quad (2.6)$$

Figure A2.1 – (top) Base particles coloured according to their $\bar{q}_6$ bond parameter. (middle) the phase diagram for our simulation system. Bottom: $\bar{q}_6$ histograms. (A) The liquid phase at $\phi = 0.060$. (B) Phase coexistence of liquid at the bcc phase at $\phi = 0.063$. (C) A bcc phase at $\phi = 0.0656$. Histograms are an average over 90 snapshots separated by $\Delta t = 2 \cdot 10^1 \tau_b$

where N_b is the number of neighbours of particle i . We identify nearest-neighbours based on proximity, considering only particles closer together than the lattice constant a . The spherical harmonic bond order parameter $q_{lm}(k)$ for particle i is given by

$$q_{lm}(i) = \frac{1}{N_b(i)} \sum_{j=1}^{N_b(i)} Y_{lm}(\mathbf{r}_{ij}) \quad (2.7)$$

where Y_{lm} are the spherical harmonics.

Using $\bar{q}_6$ we characterise the local structure. We reconstruct our in-silico system by colour-coding all particles according to their $\bar{q}_6$ value for the three different regimes: liquid, liquid–bcc coexistence, and solid bcc (Fig. A2.1A–C top). This clearly shows the different regimes in our phase diagram. In order to identify the phase transition points we calculate the probability distribution $P(\bar{q}_6)$. Here we average over 90 snapshots with $dt = 2 \cdot 10^1 \tau_b$ (Fig. A2.1A–C bottom). We find three distinct behaviours. In the liquid we observe a sharp peak around a $\bar{q}_6$ value of 0.2 (Fig. A2.1A bottom). The solid bcc (including dopants) exhibits a peak around a value of 0.4 with a tail extending towards lower $\bar{q}_6$ values, due to the dopant induced lattice strain (Fig. A2.1C bottom).

In the phase coexistence regime we observe a peak at $\bar{q}_6 = 0.4$, corresponding to the bcc crystal structure, and a large tail extending to lower values corresponding to the coexisting liquid pockets (Fig. A2.1C bottom).

We locate the melting point, where liquid pockets first appear, at $\phi \sim 0.0655$, and the freezing point, where the last remnants of solid vanish at $\phi \sim 0.0605$. These transitions are in agreement with those found in the experimental system onto which our simulation parameterisation is

mapped.

Calculation of two-dimensional structure factor

We calculate a two-dimensional projection of the three-dimensional static structure factor $S(\mathbf{q})$ as:

Figure A2.2 – $S(q_x, q_y)$ of the base particles of (A) a static base crystal with $\phi = 0.07$, (B) a dynamic base crystal with $\phi = 0.07$ and (textbfC) experimental bcc crystal with $\phi = 0.14$.

$$S(\mathbf{q}) = \frac{1}{N} \left\langle \sum_{jk} \exp i\mathbf{q} \cdot (\mathbf{r}_j - \mathbf{r}_k) \right\rangle \quad (2.8)$$

averaged over all particles and time (Fig. A2.2). We find well defined Bragg peaks corresponding to a bcc crystal for the static base crystal, the dynamic base crystal, and the experimental bcc phase system.

Percolating network of tetrahedral interstitial sites

Figure A2.3 – Base particles (blue) with an isosurface (orange) plotted of the potential field felt by a dopant particle. (A) Static base crystal with isosurface at $\Delta U = 3.5 \text{ k}_B T$ and (B) potential field of a snapshot at $t = 2 \cdot 10^3 \sigma_b$ with an isosurface at $\Delta U = 42 \text{ k}_B T$.

To illustrate the percolated network of tetrahedral hopping transitions we plot an isosurface ($U(\mathbf{r}) = 3.5 \text{ k}_B T$) of the calculated three-dimensional potential field for the static base crystal (Fig. A2.3A). The interconnected transition path network can be clearly seen. By contrast, a similar analysis for the fluctuating dynamic base crystal ($U(\mathbf{r}) = 42 \text{ k}_B T$), reveals a striking difference with a complete vanishing of the interconnected structure, and only localised blobs of lower potential energy remaining (Fig. A2.3B). Both potential fields are calculated on simulation snapshots of the system on a grid of $100 \times 100 \times 100$ voxels.

Influence of dopants on base crystal structure

Figure A2.4 – The $\bar{q}_6$ versus $\bar{q}_4$ for every particle in a snapshot of the system at $t = 2 \cdot 10^3 \tau_b$. for **(A)** a static base crystal at $\phi = 0.07$ and **(B)** a dynamic base crystal at $\phi = 0.07$. **(C)** The probability distribution for $\bar{q}_6$ in a system without dopant particles (left) and $N_d : N = 1:47$ (right). This is an average over 90 snapshots separated by $\Delta t = 2 \cdot 10^1 \tau_b$.

In order to determine the local structure of the bcc phase we plot the average bond parameters $\bar{q}_4$ and $\bar{q}_6$ for every base particle (blue) and every dopant (green), for both a static base crystal (Fig. A2.4A left) and a dynamic base crystal (Fig. A2.4A right). As a reference we have plotted $\bar{q}_4$ and $\bar{q}_6$ for particles in a perfect bcc lattice (red) and particles in a liquid state (yellow, obtained from simulations at $\phi = 0.600$).

The fact that the structure of the base crystal is influenced by thermal fluctuations is apparent from the $\bar{q}_6$ bond parameter probability distribution (Fig. A2.4B). The addition of dopants results in the appearance of a tail in $P(\bar{q}_6)$ at $\bar{q}_6 < 0.46$, indicating that the dopants locally strain the bcc lattice (Fig. A2.4B).

Determination of the long time diffusion coefficient

The dynamics of the dopant particles are studied by means of their mean-squared displacement $\langle \Delta r^2 \rangle$. For every particle we calculate $\langle \Delta r^2 \rangle$ from the dopant particle trajectories for 200 values of τ logarithmically spaced over the entire simulation duration. In addition, we perform an ensemble-average over all particles, for both static (Fig. A2.5A red curves) and dynamic (Fig. A2.5A blue curves) base crystals. We define an effective diffusion rate as the local slope of the mean-squared displacement $D = \frac{1}{6} \frac{d\langle \Delta r^2 \rangle}{d\tau}$ (Fig. A2.5B). To extract the long time diffusion coefficient D_l we use two methods: First we take D_l to be the diffusion coefficient at $\tau = 5 \cdot 10^2 \tau_b$. Secondly we fit the tail-end of the $D(\tau)$ curve with the function $D(\tau) = -1 + c^{\frac{1}{\tau}} + D_l$, where both c and D_l are used as fit parameters. The values found for D_l using both methods are in

Figure A2.5 – Ensemble averaged mean-squared displacements for all volume fractions, $\phi = 0.0656, 0.066, 0.067, 0.070, 0.071, 0.075, 0.08, 0.09, 0.10, 0.12, 0.15$, and 0.20 . **(A)** $\langle \Delta r^2(\tau) \rangle$ of the dopant particles for a static base crystal (red) and a dynamic base crystal (blue). Volume fraction increases from bottom to top **(B)** The diffusion coefficient $D(\tau)$ calculated from the gradient of $\langle \Delta r^2(\tau) \rangle$ for the static base crystal (red), the dynamic base crystal with $N_d : N = 1:47$ (blue). ϕ decreases from bottom to top. **(C)** Ensemble averaged mean-squared displacements for a longer simulations; the extra order of magnitude in simulation time clearly shows the upturn towards diffusive behaviour; dashed line has a slope of one.

close agreement (Fig. 2.4A blue open & closed triangles). To show that at long times the MSD goes towards diffusive behaviour we performed an extended simulation. The mean-squared displacements calculated from this simulations clearly show the upturn at long times towards a slope of one; indicative of diffusive motion (Fig. A2.5C).

Voronoi analysis

Figure A2.6 – Results from Voronoi analysis on dopant particles at $\phi = 0.07$ for a static base crystal (red) and a dynamic base crystal (blue) **(A)** The average voronoi volume, **(B)** the voronoi volume at a snapshot at $t = 2 \cdot 10^3 \tau_b$ and **(C)** the number of faces at $t = 2 \cdot 10^3 \tau_b$.

To evaluate the local environment of dopant particles, we use a Voronoi analysis; we calculate Voronoi cells using voro++[32] taking into account the periodic boundaries of our simulation box. We observe a significant difference in the local environment of the dopant particles in the static base crystal compared to the dynamic base particles. In the case of a static base crystal the distribution in Voronoi volume is very narrow both averaged over time and in a simulation snapshot (Fig. A2.6A–B red). The dynamic base crystal case shows a much larger distribution of Voronoi

cell volumes (Fig. A2.6A–B blue), again confirming the highly heterogeneous nature of the instantaneous structure of soft bcc crystals. We also compare the number of faces of a Voronoi cell around a dopant for the cases of a static and a dynamic base crystal. For a dopant which resides at the tetrahedral site in a perfect bcc crystal the expected number of faces is 8; this is indeed what we find in a static crystal (Fig. A2.6C red), confirming that virtually all interstitial dopants reside in tetrahedral sites. The few cells which exhibit a higher number of faces correspond to dopants which are in transition between two tetrahedral sites since these data are taken from snapshots of the dopant structure. The situation in the dynamic crystal is significantly different, the loss of well defined interstitial sites causes the dopant particles to have a Voronoi cell faces distribution close to what we would expect for the base particles in a regular bcc lattice site (Fig. A2.6C blue).

Clustering of interstitial dopants

Figure A2.7 – Cluster analysis at different volume fractions: **(A)** $\phi = 0.07$, **(B)** $\phi = 0.09$, **(C)** $\phi = 0.15$ and **(D)** $\phi = 0.20$. Systems all have $N_d : N = 1:47$. Top: Snapshots of cluster formation at $t = 2 \cdot 10^3 \tau_b$, only the clusters with $S_C \geq 4$ are highlighted for clarity. Middle: $\langle \Delta r^2(\tau) \rangle$ curves per particle (grey) and the ensemble average (red). Bottom: Histograms of the $\langle \Delta r^2 \rangle$ at $\tau = 5 \cdot 10^2$ over 50 bins.

Clustering occurs across the whole range of volume fractions for dynamic base crystals (Fig. A2.7A–D top row), whereas it remains completely absent for the fixed base crystals. Clusters are identified using the DBSCAN algorithm as developed by Ester et al.[40] and embedded in the python library scikit-learn. We consider particles with a maximum nearest neighbour distance of $1.5 a$ to be in a single cluster, where a is the lattice constant and the minimum cluster size is two. The heterogeneity in local cluster distribution is also reflected in the single-particle mean-squared displacements of the dopants. To this end we plot the

distribution of $\langle \Delta r^2(\tau) \rangle$ values for all dopants in the simulation system (Fig. A2.7A–D middle row). The distribution of MSD curves is highly heterogeneous, with different populations of dopant particles with similar MSD curves visible as thick bundles. To more clearly illustrate the heterogeneity of the MSD distribution we plot a distribution of $\langle \Delta r^2(\tau/\tau_b = 5 \cdot 10^2) \rangle$ (Fig. A2.7A–D bottom row), which indeed shows multiple populations, which we attribute to singlets and clustered dopants.

Heterogeneous long time dynamics.

Figure A2.8 – $\langle \Delta r^2 \rangle$ at $t = 5 \cdot 10^2$ versus the fraction of simulation time that a particle is part of a cluster. Plotted for volume fractions: **(A)** $\phi = 0.07$ and **(B)** $\phi = 0.12$.

To investigate the cause of dynamical heterogeneity on long time scales we calculate the fraction of time a particle is present in a cluster. This fraction is plotted against $\langle \Delta r^2 \rangle$ at $\tau/\tau_b = 5 \cdot 10^2$ for every particle. This shows that at both high and low volume fractions there are two groups: clustered particles and singlets (Fig. A2.8A & B). Singlets only show low $\langle \Delta r^2 \rangle$ values, indicating strong localisation of singlets, while clustered particles show a broad range in these values. It is clear that at low volume fractions of the base crystal, where the elastic interactions responsible for clustering are weaker, the exchange of particles between singles and clusters is more dynamic, thus reducing the average time a particle resides in a clustered configuration.

Cluster dynamics

We start by looking at the fraction of total dopant particles in the system that are part of a cluster as a function of volume fraction ϕ (Fig. A2.9A). The difference between the two states of the base crystal (static or dynamic) is striking. For the dynamic case we see that most of the particles form part of cluster and this ratio doesn't change significantly with ϕ (Fig. A2.9A blue circles). For the fixed base crystal, the number of particles forming part of a cluster of $N \geq 2$ is very low and drops off as ϕ increases (Fig. A2.9A red triangles). This seems to suggest that the

Figure A2.9 – (A) The average fraction of clustered particles N_C/N against ϕ . (B) Averaged cluster size S_C as a function of ϕ and (C) average amount of clusters C_N against ϕ . For $N_d : N = 1:47$ in a static base crystal (red triangles) and in a dynamic base crystal (blue circles) (D–F) Behaviour of N_C/N , $\langle S_C \rangle$, and C_N during the simulation at two different volume fractions $\phi = 0.07$ (blue circles and red downward pointing triangles) $\phi = 0.12$ (blue squares and red upward pointing triangles).

clusters formed in the static case consist mostly of dimers due to the random thermal distribution of dopants across the lattice.

Over time the fraction of particles present in a clustered, versus a singlet, state is constant (Fig. A2.9D–F). For the dynamic crystal we observe small fluctuations in the fraction of clustered dopants around a mean value, indicative of the dynamic equilibrium between clusters and singlets. For the static cases these fluctuations are larger, as a result of the fact that these clusters are not formed by an effective medium attraction, driven by a minimisation of the lattice strain but simply by random collisions of dopant particles as they diffuse across the lattice.

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DOPING COLLOIDAL BCC CRYSTALS — INTERSTITIAL SOLIDS AND META-STABLE CLUSTERS

3

The addition of a small amount of dopant impurities to crystals is a common method to tune the properties of materials. Usually the doping grade is restricted by the low solubility of the dopants; increasing the doping concentration beyond this solubility limit leads to supersaturated solutions in which dopant clusters dominate the material properties, often leading to deterioration of strength and performance. Descriptions of doped solids often assume that thermal excitations of the on average perfect matrix are small. However, especially for bcc crystals close to their melting point it has recently become clear that the effects of thermal disorder are strong. Here we study the doping of weak bcc crystals of charged colloids via Brownian dynamics simulations. We find a complex phase diagram upon varying the dopant concentration. At low dopant concentrations we find an interstitial solid solution. As we increase the amount of dopants a complex meta-stable liquid-in-solid cluster phase emerges. Ultimately this phase becomes meta-stable with respect to macroscopic crystal-crystal coexistence. These results illustrate the complex behaviour that emerges when thermal excitations of the matrix drive impure crystals to a weak state.

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“Doping colloidal bcc crystals — interstitial solids and meta-stable clusters”

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Introduction

A COMMON approach to tune the properties of crystalline solids is the process of doping; the introduction of interstitial atoms in a crystalline matrix with the purpose of changing the materials properties. The canonical example of this process is the addition of small amounts of carbon as an interstitial dopant in an iron matrix to toughen the material and create steel. The movement of Li-ions through an inorganic matrix in superionic solid-state batteries, such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$, is also a form of interstitial doping since the Li-ions move through the lattice via a percolating network of interstitial sites [1, 2]. In the case of Fe, the addition of too much carbon, e.g. in cast iron, makes a very brittle substance. Clearly the properties of doped crystalline materials are highly dependent on the degree and distribution of dopants. The solubility limit of dopants is often very low; e.g. 0.022 wt % for carbon in α -Fe at 723 °C [3]. With the addition of additional dopants beyond this point precipitation of the alloy occurs[4] and material properties degrade. Due to the small length scales inherent in the study of atomic materials, the process of crossing the solution limit; going from a low concentration of dopant to a supersaturated solid solution, has not been investigated on a single particle level. Models and experiments have found evidence for dopant clustering and the formation of dopant rich domains in supersaturated interstitial alloys [5, 6, 7, 8]. However, due to the inherently short time and length scales involved in atomic materials, investigation into supersaturated solid solutions on a single particle level is very difficult. To overcome this limitation we explore the use of colloids as a model system for impure crystals; these systems are easily observed with microscopy techniques and show behaviour that in some cases is analogous to their atomic counterparts[9].

While pure colloidal crystals have been studied in detail, much less is known about impure crystals. Binary systems, that is systems which consist of two particle species with a high size asymmetry such as doped crystals, show a complicated phase diagram identified using both experiments [10, 11, 12] and simulations [13, 14]. However, so far research has focused on hard-sphere colloidal systems, which only exhibit a face-centred cubic (fcc) structure. This is in contrast with many metals which have body-centred cubic (bcc) crystal symmetry, especially at conditions used for processing, temperatures at or slightly below their melting points [15].

Colloidal systems of charged spheres where interactions take the form of long ranged repulsive Yukawa pair-potentials, show a much richer phase behaviour, exhibiting a low density bcc phase. This model for weak bcc crystals is akin to those found in electron systems [16], neutron stars [17], and dusty plasmas [18]. These very soft bcc lattices are unique as their transition into the liquid is weakly first order [15]. Recent experimental work has evidenced the weak first-order transition and entropic stabilisation of weak bcc crystals and shown that this leads to a failure of classical lattice theory [19]. Rather, strong thermal disorder and large correlated fluctuations govern the crystal physics. This has some unusual effects on the properties of the crystalline solid that, while ordered on average, displays some features typically associated with disordered solids, such as a elasticity that is governed by non-affine fluctuations, leading to a breakdown of the Born–Huang lattice dynamics [19, 20, 21, 22].

Since the elasticity in these thermally-disordered crystals becomes governed by non-affinity and the classical rules of crystal lattice dynamics fail, one may also expect that doped crystals would behave anomalously. It is the weakness of these bcc crystals which also results in a unique behaviour when they are doped. We have previously shown that the large off-lattice fluctuations are the reason existing theoretical predictions for dopant dynamics break down [23]. Firstly the large thermal excitations of the bcc lattice, destroy the percolating path of interstitial sites and significantly restrict the motion of interstitial dopants through the crystal. Secondly, the lattice deformation that results from the introduction of a dopant mediates an effective attractive interaction between the dopants. At the low doping levels studied, small clusters were observed as a result of this, again restricting the diffusion of dopants, this time due to the formation of clusters. So far only low doping levels have been investigated; this raises the inevitable question of what happens when doping concentrations reach supersaturated levels, where for atomic solids it is known that material properties rapidly change — such as a notably lower rate of diffusion similar to what we observed in colloidal systems [24].

In this chapter we study, using Brownian dynamics simulations, the behaviour of weak bcc crystals of repulsive Yukawa particles, doped with a wide range of doping fractions. We identify a transition, with increasing number of added dopants, from an interstitial solid-solution phase, **ISS**, to a meta-stable phase of phase-separated liquid pockets, **XLP**. This phase is a coexistence of a crystalline base particles phase with spherical pockets of liquid dopants. At higher dopant concentrations we find a second transition where the liquid-pockets fuse and a macroscopic crystal-liquid, **XL**, coexistence emerges. As we reach the highest dopant concentrations, the local volume fraction of the dopant phase crosses its melting point and we find a crystal plus meta-stable liquid, **XML** phase.

The meta-stable liquid will, given enough time, crystallise, resulting in complete crystal-crystal phase separation, **XX**. These results give new insights into the complex phase behaviour of impure colloidal crystals.

Results and Discussion

We simulate a base crystal consisting of 13718 particles with diameter, $\sigma_{base} = 1.8 \mu\text{m}$, at a volume fraction $\phi_{base} = 0.10$ inside a box of length $L_x = L_y = L_z = 41.57 \sigma_{base}$ with periodic boundary conditions. These bcc crystals are doped with particles with diameter $\sigma_{dopant} = 0.9 \mu\text{m}$. The resulting size ratio $\rho = \frac{\sigma_{base}}{\sigma_{dopant}} = 0.5$ is close to that of carbon in iron [25]. The concentration of dopants is our variable, expressed as a fraction of the total available tetrahedral interstitial sites (Fig. 3.1) in the base crystal which are occupied. We call this the interstitial fraction, **IF**. Since there are 12 tetrahedral interstitial sites per unit cell in a bcc crystal **IF** = 1.0 would equal 82308 dopants divided over 6859 unit cells.

Figure 3.1 – (A) Computer rendering of a body-centred cubic (bcc) unit cell (purple, large spheres) and locations of the tetrahedral interstitial sites (orange, smaller spheres); of which there are four on each face of the unit cell (twelve per unit cell). (B) Computer rendering of a body-centred cubic (bcc) unit cell (purple, large spheres) and locations of the octahedral interstitial sites (yellow, smaller spheres); of which there is one on each face of the unit cell and one on each edge (six per unit cell). (C) If we ignore the dynamics of the base crystal particles the dopant particles are distributed homogeneously throughout the crystal. (D) Due to matrix mediated effective attractive interactions between dopants we observe clusters and phase separated liquid pockets in systems where we do take into account the influence of base particle dynamics.

In doped crystals the impurities will, if small enough, position themselves in the lowest-energy interstitial sites of the surrounding crystal matrix. In the case of a perfect bcc crystal we can identify two types of interstitial sites; tetrahedral (Fig. 3.1A) and octahedral sites (Fig. 3.1B), so named after the number of faces of the polyhedron created by treating the nearest-neighbour matrix particles as vertices. These sites form the local minima in the potential field created by the base crystal particles. Dopants prefer to reside in the tetrahedral sites because these have the lowest potential energy of the two different types. In bcc crystals dopant diffusion between tetrahedral interstitial sites has classically been described as a thermally-activated hopping process governed by the energy barrier, U_A between two adjacent sites. Within this approach it is assumed that the potential energy field that a dopant experiences is static and prescribed by a perfect lattice, and that interactions between dopant particles are negligible. In a previous paper, we showed that dopant dynamics in soft crystals approaching their melting point, $\phi \sim \phi_{melt}$, can not be adequately described by theories based on these assumptions. Long-time diffusion coefficients for the dopants are two orders-of-magnitude lower than those predicted based on the idealised energy landscape. However, in both situations diffusion through the lattice is still faster than in hard sphere systems [10]. When we take thermal motion of the base crystal into account, the well-defined local minima in the potential energy landscape disappear due to strong excitations of the marginally-rigid crystal, such that well-defined interstitial sites can no longer be identified from snap-shots of the structure. The percolating path of tetrahedral sites is broken, which prevents interstitial particles to diffuse effectively throughout a bcc crystal; significantly lowering their long-time diffusion coefficients.

Another factor slowing down the dopant diffusion is the emergence of attractive dopant-dopant interactions, even though all pair interactions in our system are repulsive. The introduction of dopants into the crystal leads to a small deformation of the lattice. The lattice strain is minimised by clustering dopants [26], resulting in emergent elastic interactions between dopants. These effects have recently been proven in experiments on colloidal hard sphere crystals; showing how a stress field emerging from a point defect causes relatively long ranged defect-defect interactions [27].

In our simulations, these effects are evident when we compare dopants in a thermal and a static base crystal. With a static base crystal we find the dopants distributed homogeneously throughout the bcc lattice over all available interstitial sites. Switching the thermal excitations of the base crystal on results in clustering of dopants due to the emergence of attractive forces between the dopants (Fig. 3.1C and D). So far we have only investigated systems in the low doping limit, thereby minim-

ising dopant-dopant interactions. As the amount of dopants increases, a complex phase behaviour appears. The doping degree is expressed as the fraction of tetrahedral interstitial sites that have a dopant particle present at the beginning of our simulations called the interstitial fraction **IF**, ranging from 0.0 for zero doping to 1.0 when all tetrahedral interstitial sites (12 per unit cell) are filled. At the lowest **IF** we simulate, 0.01, the dopants are spread evenly over the entire bcc crystal; an interstitial solid solution, **ISS**, similar to what has been found for doped hard sphere crystals [10, 28, 29]. In doped hard sphere systems when the dopant diameter, σ_D , is smaller than or equal to the largest interstitial site — octahedral sites for fcc crystals, σ_{IS} — i.e. $\sigma_D \leq \sigma_{IS}$, there is no lattice strain induced by the introduction of the interstitial impurity. In this case, in absence of enthalpic interactions, there is no cause for clustering. If the hard-sphere interstitial is larger than the interstitial site, lattice strain accompanies the doping, for example for the particular case of self-interstitials, clustering occurs at sufficient doping fractions [30]. By contrast, for the Yukawa system, even dopants that geometrically fit into the interstitial void spaces exert enthalpic forces onto the surrounding matrix, causing a deformation of the crystal and providing a mechanism for attractive dopant–dopant interactions. Indeed, we observe the presence of a few small clusters of dopants even at the lowest **IF** (Fig. 3.3A & Fig. 3.2 example I).

Based on an analysis of the averaged local bond-orientational order parameter $\bar{q}_6$ of the dopant-dopant structure, we conclude that the majority of these clusters have an internal bcc symmetry, as evident from the orientational bond-order parameter $\bar{q}_6 \approx 0.4$ (see Methods), and therefore represent clusters of interstitial particles. A minority of clusters have $\bar{q}_6$ values in the range we expect for liquids ($\bar{q}_6 \approx 0.2$) [31]; these clusters consist of phase separated dopant particles forming a small liquid pocket in the bcc base crystal. The presence of dopants in two states is confirmed by the structure factor $S(q_x, q_y)$ of both the base particles and dopants. The bcc symmetry of the base crystal is clearly reflected in the calculated diffraction pattern (Fig. 3.3B). For the dopants we see blurred bcc reflections, with a sharp peak in the middle, the result of dopant particles at their tetrahedral interstitial sites combined with the few small liquid-pockets (Fig. 3.3C). We note that the use of the orientational bond-order parameter only probes the local and static structure of the solid and has no bearing on possible anomalies that may emerge in these solids due to non-affinity in their mechanics and dynamics [19, 32]. However, since these latter are not part of the topic of this study, the static bond order parameters provide us insight into the local particle symmetry.

With increasing **IF** the system transitions into a cluster phase characterised by pockets of dopant liquid in a crystalline bcc matrix (Crystal + Liquid Pockets, **XLP**) (Fig. 3.3D). The transition from an **ISS** to a **XLP**

Figure 3.2 – We show the evolution of the fraction of interstitial dopants (blue circles) and phase separated dopant particles (red circles) as a function of the total amount of dopant particles in the system; expressed as the fraction of tetrahedral interstitial sites filled at the start of the simulations, $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$, & 0.30 . The triangular symbol indicates the one sample we found which showed predominately bcc symmetry in the dopant phase. We describe four distinct regimes as indicated with roman numerals in the figure. **(I)** A transitional regime from a phase dominated by dopants acting as an interstitial solid solution towards a phase of dopants phase separated into liquid clusters or into a single liquid phase **(II)**. **(III)** In this regime the volume fraction of the dopant phase has increased above melting point ($\phi_m \approx 0.031$) for a dopant only system (dashed vertical line) and we find meta-stable liquid, crystalline **(IV)** or mixed dopant phases. **(top row)** Visual illustration of the different regimes identified. We have rendered the dopant particles at twice their size and coloured them according to their bond-orientational order parameter, $\bar{q}_6$.

phase is a gradual process — the amount of dopants in the solid solutions decreases while the number of dopants part of a liquid-cluster increases over the range $0.01 < IF < 0.04$ (Fig. 3.2). The liquid structure of the dopant pockets is corroborated by the calculated diffraction patterns, calculated separately for dopant-dopant and base-base structure, which show clear Debye–Scherrer rings associated with liquid order (Fig. 3.3F). These liquid pockets have internal volume fractions in the range of $\phi_L = 0.017$ to $\phi_L = 0.04$ which is below the volume fraction needed for vitrification. We therefore attribute the diffraction rings to a liquid and not to a glass phase. The presence of liquid clusters disrupts the bcc lattice of the matrix in such a way that the distinct Bragg reflections disappear

Figure 3.3 – (top row) Computer renderings of final simulation snapshots of simulated doped bcc crystals. With base crystal particles in purple and dopants in yellow. From left to right the dopant interstitial fraction, IF , increases ($IF = 0.01, 0.05, 0.20, \& 0.25$) and transitions from an interstitial solid solution, to phase separated liquid pockets of dopants, and finally towards a fully phase separated crystal-crystal system. **(middle row)** Two-dimensional structure factors $S(q_x, q_y)$ calculated from particle centre-of-masses for base particles only. Even though the base crystal lattice is highly disrupted by the liquid clusters, the visibility of Bragg peaks over the entire IF range indicates the continual presence of local crystalline domains in the system. **(bottom row)** Two-dimensional structure factors $S(q_x, q_y)$ calculated from particle centre-of-masses for dopant particles only. There is clear transition from visibly though smeared-out peaks in the interstitial solution, *ISS*, phase at low IF into a dopant liquid pocket, *XLP*, phase which finally at the point of full phase separation crystallises.

from their diffraction pattern. The clusters appear to act as nuclei for grain boundaries; the diffraction pattern of the base crystal reflects its poly-crystalline nature. The grains still have an internal bcc symmetry as shown by the radial distribution function, $g(r)$ and the distribution of the bond-orientational order parameter, $\bar{q}_6$ (See Appendix, Fig. A3.1A–Fig. A3.3).

The distortion of the bcc matrix, upon increasing the amount of dopants and the emergence of liquid pockets, results in a superposition of scattering patterns with different spatial orientations (Fig.3.3E &

H) with excess Bragg peaks as a result. However, analysis of the bond-orientational order parameters $\bar{q}_6$ and $\bar{q}_4$ (See Appendix, Fig. A3.2–A3.5) reveals that the local bcc symmetry is maintained, since their values are consistent with the body-centred cubic lattice and rule out other symmetries observed in these types of systems such as the face-centred cubic (fcc) or hexagonal close packed (hcp) lattices.

The evolution of an **ISS** towards stable pockets of dopant liquids is a unique feature of doped weak crystals. Recent work on hard sphere doped systems shows the co-crystallisation of **ISS** phases with up to ~14% of octahedral sites filled by dopants [29], corresponding to $\text{IF} \approx 0.058$ in our bcc systems. This is a bit higher than the point where all **ISS** dopants have disappeared and the system has fully converted to pockets of dopant liquid suspended in a bcc crystal, $\text{IF} \approx 0.04$. In doped hard sphere fcc crystals at close-packing, the diffusion of dopants is effectively nullified. However, at slightly lower volume fraction there is dopant diffusion by hopping between interstitial sites, crossing a free energy barrier [10]. By contrast, the weak bcc lattice, $\phi_{base} = 0.1$, allows for faster dopant diffusion when compared to a hard-sphere matrix.

So far we have observed a transition of an interstitial solid solution into a phase where the dopant particles have phase separated into a number of clusters with a liquid internal structure — upon increasing IF from 0.01 to 0.04. As the amount of dopants increases further, $\text{IF} \geq 0.05$, the size of the dopant clusters increases while their number decreases (Fig. 3.4) until the system separates into two distinct phases of a bcc matrix crystal of large particles and a liquid of dopants, a crystal-liquid coexistence **XL**. For $\text{IF} > 0.10$, the separated and kinetically stable pockets merge into a single phase (Fig. 3.3G, H, & I).

Over the entire IF range there is an increase in the internal volume fraction of the phase-separated liquid dopant phase, ranging from $\phi_L = 0.01769$ at $\text{IF} = 0.01$ to $\phi_L = 0.04092$ at $\text{IF} = 0.30$ (Fig. 3.5A). This raises the question whether in the phase separated dopant phases we are dealing with volume fractions above or below the melting point, ϕ_m , of the equivalent system of only small dopant particles. To find the phase boundaries of a pure dopant system we simulate a system with as an initial condition a box filled half with a bcc crystal and half with randomised positions, at a fixed volume fraction. With this method, with both of the possible end configurations present at the start, we can easily determine which phase starts to dominate during the simulation and is thus the lowest free energy state. We find the melting point for the pure dopant system at $\phi_m \approx 0.03125$ (Fig. 3.5A, dashed line). Below this point the system relaxes into a liquid while at $\phi > \phi_m$ the system has a bcc crystal configuration as its equilibrium state. If we repeat the simulations with systems which have a fully liquid or crystal initial configuration we do not observe melting or freezing, suggesting that nucleation is rare and slow in these systems.

Figure 3.4 – (A) The number of dopant particles involved in a cluster divided by the total number of dopant particles, n_c/N , as a function of the number of dopant particles; expressed as IF . (B) Renderings of dopant clusters at the end of simulations for $IF = 0.01, 0.03, 0.05, \& 0.10$. (C) Number of clusters present in a system for the last $1000 \tau_B$ of the simulation. Different symbols represent different values for IF . (D) Size of clusters, averaged over all clusters present in a system, for the last $1000 \tau_B$ of the simulation. Different symbols represent different values for IF increasing from top to bottom for (C) and increasing from bottom to top for (D). Values of IF are those reported in the Methods section.

With the dopant freezing point at $\phi_m \approx 0.031$ the dopant phase in most of our simulations are in its liquid state. However, for those systems where $\phi_L > \phi_m$, occurring for $IF > 0.15$, we would expect, based solely on the local volume fraction, to find a crystalline dopant phase. We observe different degrees of crystallinity in the dopant phase for $IF = 0.20, 0.25, 0.27, \& 0.30$ based on their bond-orientational order parameter, $\bar{q}_6$. This finding is corroborated by the probability distribution for the bond-orientational order parameter $P(\bar{q}_6)$; at these dopant fractions we observe a non zero probability of $\bar{q}_6 \approx 0.4$, the expected value for a bcc symmetry (Fig. A3.3 in the Appendix) [31]. The presence of local bcc order suggests that the dopant phase is definitely in a regime where it wants to crystallise, but is hindered in doing so to the fullest extent, possibly by the irregularity of the dopant-base interface. The crossing of the dopant melting point introduces a new transition, from a crystalline matrix separated from a liquid dopant phase, **XL**, into a meta-stable liquid dopant phase, **XML**.

The rich phase behaviour of our system is summarised in Figure 3.2. We plot the fraction of interstitial dopants and the fraction of separ-

Figure 3.5 – (A) The change in the local volume fraction, calculated via voronoi tessellations, of dopants belonging to the phase separated phase as a function of the number of filled tetrahedral interstitial sites. The red lines are linear fits to the two distinct behavioural regimes as explained in the text. The dashed line indicates the approximate melting point, ϕ_m of a dopant only system. (B) The distribution of the bond-orientational order parameter, $\bar{q}_6$, for a system at a volume fraction $\phi_L = 0.03220$ ($IF = 0.175$). Calculated for the sides of the system which at the start of the simulation were either a bcc crystal (red circles) or a liquid (blue triangles). The black lines indicate the original distribution of $\bar{q}_6$ at the start of the simulations. (C) The distribution of the bond-orientational order parameter, $\bar{q}_6$, for a system at a volume fraction $\phi_L = 0.03052$ ($IF = 0.15$). Calculated for the sides of the system which at the start of the simulation were either a bcc crystal (red circles) or a liquid (blue triangles). The black lines indicate the original distribution of $\bar{q}_6$ at the start of the simulations.

ated dopants as a function of the total dopant concentration. We count both single dopants and clustered dopants with a cluster-averaged $\bar{q}_6 > 0.4$ — indicating the cluster has bcc symmetry — as interstitial dopants. Two stages are observable. First the number of interstitial solid solution dopants (ISS; Fig. 3.2 example I) decreases as the total amount of dopants increases until we are left with a system where all dopants have phase separated from the base crystal in the form of liquid pockets (XLP; Fig. 3.2 example II). This first stage is followed by growth of the pockets until a single dopant phase has formed (XL), the doped system has at this point effectively separated into two phases. These distinct phases of separation and growth can also be observed in the increase of the local volume fraction of the phase separated dopants; there is a distinct kink at the point where the population of interstitial dopants ceases to exist (Fig. 3.5A points and solid lines). Finally the liquid dopant phase undergoes one more internal transition from a liquid into a meta-stable liquid (XML; Fig. 3.2 example III), with the occasional occurrence of a crystal-line dopant phase (XX; Fig. 3.2 example IV). The full phase separation of a binary system is predicted by thermodynamical models. However, the appearance of phase separated distinct clusters which are stable in time is unusual. We find that larger initial dopant concentrations lead to larger final clusters. For clusters in equilibrium we would expect that the cluster formation is reversible; lowering the number of dopants in a

clustered configuration would result in the breakup of the larger clusters into smaller ones. To this end we start simulations from the final state of a simulation and remove a number of randomly selected dopants such that IF drops from 0.20, a single large cluster, to 0.10, multiple smaller clusters. For an equilibrium phase we would expect the large cluster to break-up into a multitude of smaller ones. This does not seem to be the case; instead the single large cluster compresses due to the expanding base crystal matrix (Fig. 3.6 & 3.7) — we are not dealing with an equilibrium phase but a kinetically trapped phase.

To evaluate the stability of these kinetically trapped liquid clusters we measure the total number of clusters and the average size of those clusters over time. There are two possible coarsening modes for established clusters: either through Ostwald ripening, which would involve the transfer of particles from one cluster to another, or through coalescence — the merging of multiple clusters to form bigger ones. Coarsening through Ostwald ripening scales with the surface energy, $\gamma_{d,b}$, between the dopant phase and base matrix. We calculate both the systems total potential energy, U and the surface area, A between dopant and matrix phases for the final 750 τ_B of our simulation; plotting the energy versus the area and fitting with a linear function, $U \propto \gamma_{d,b} A$ gives us an indication of the enthalpic surface energy in our system. We find $\gamma_{d,b} = 4 k_B T \sigma^{-2}$ (see Appendix Fig. A3.6), this low value on the order of $k_B T$ makes it unlikely that Ostwald ripening is the driving force behind possible dopant droplet coarsening. The other option would be coarsening through merger events, this process relies on the ability of clusters to efficiently diffuse through the matrix in order to meet and merge. This seems highly unlikely, since all clusters appear to be kinetically trapped during our simulation (See Appendix for cluster centre-of-mass mean-squared displacements, Fig. A3.7). We therefore expect very little, if any, change in the average size of clusters once they are established. Indeed, during the last 1000 τ_B there is no discernible change in cluster numbers or average size (Fig. 3.4C & D).

In doped crystals of hard spheres, where the volume fraction goes above fcc close packing since the dopants fill in the interstitial spaces, dopants diffuse through the lattice at a much slower pace when compared to a weak bcc crystal [10, 23]. The diffusion from one interstitial site to the next involves the crossing of an energy barrier set by surrounding base particles. In the case of a hard sphere fcc packing of the base crystal this energy barrier is on the order of several $k_B T$ and has to be crossed twice because hopping goes through an interstitial site of the opposite type, i.e. the transition from one octahedral site to the next goes through a neighbouring tetrahedral site. For weak bcc crystals the strongly increased fluctuations in the base crystal and the, in general, much lower volume fraction allows for far higher dopant diffusion rates when compared to

Figure 3.6 — Reverse simulation — initial state

Figure 3.7 — Reverse simulation — final, isotropically compressed, state

Figure 3.8 – (A–N) Mean-squared displacement distributions, $P(\Delta r^2(\tau = \tau_L))$, with $\tau_L = 391 \tau_B$ for $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$ & 0.30 . Here angled brackets represent time averages. (O) Ensemble averaged dopant mean-squared displacement. Shown for, bottom to top, $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$ & 0.30 . Here angled brackets represent time and ensemble averages. The dashed line is a line with a slope of one. (inset) Square root of the mean-squared displacement plateau height at $\tau = 391 \tau_B$.

an equivalent hard sphere system; in order to quantify this for our system we calculate the mean-squared displacement (MSD) of each dopant during the entire simulation after equilibration. We can classify the ensemble means of the dopant MSDs in roughly two categories; those systems where the dopants have separated into a number of finite-sized domains, the liquid pockets, and those where there is a single, continuous dopant phase present (Fig. 3.8O). Both domains have the expected vibrational displacements at short time-scales, $\tau < 0.3 \tau_B$, where τ_B is the Brownian self-diffusion time of the larger base particles, and a diffusive regime at intermediate time-scales, $\tau \approx 10 \tau_B$. However, at longer times they differ. Whereas in the second category the diffusive regime persists for an extended period. Systems of the first category have an anomalous plateau at long times — the result of the finite dopant-domain size. The square-root of the height of this plateau represents the mean size of the dopant pockets, $\delta_S = \sqrt{\Delta r^2(\tau = 391 \tau_B)}$, which increases with increasing IF (Fig. 3.8O inset). This is in agreement with our visual observation of growing dopant cluster sizes with increasing IF (Fig. 3.4A). Of course, at infinitely long time-scales all MSDs should display purely diffusive behaviour with a slope of one due to the diffusion of entire dopant droplets. Running simulations long enough to capture this behaviour would take a prohibitively long time; a first indication of this upturn towards a slope of one can be seen in the curve representing $IF = 0.01$ (Fig. 3.8O bottom curve).

While the ensemble average MSD already gives us an indication of the behaviour of our doped crystals, the strength of our approach lies in the single-particle level information available. Therefore we also calculate the distribution of mean-squared displacements on a single particle level, $P(\Delta r^2(\tau = \tau_L))$ at long times, $\tau_L = 391 \tau_B$. In these distributions there is reflected the same transition, from an interstitial solid solution phase into a phase consisting of separated liquid pockets, as we have previously seen in figure 3.2 & figure 3.5. The indicator is the presence of a sharp peak in the MSD distribution in samples with low **IF** which represents dopant particles acting as interstitial dopants with an effective caging plateau around $\tau = 0.2 \sigma^2$, where σ is the diameter of the larger base particles. (Fig. 3.8A–C). With the disappearance of this peak the distribution shift to higher values, coinciding with the up shifting of the confinement plateau described above (Fig. 3.8D–G). Using both the ensemble averaged and single mean-squared displacements we identify two transitions; i.e. the transition from an interstitial solid solution into a phase consisting of finite sized pockets of liquid dopant, followed by a second transition from finite-sized pockets towards a system spanning single dopant phase. The first transition occurs in the range $0.01 < \mathbf{IF} < 0.04$ with the second taking place between $\mathbf{IF} = 0.10$ and $\mathbf{IF} = 0.125$.

The high mobilities of dopants before clustering has taken place in these weak bcc crystals especially when compared to binary hard sphere systems is the determining factor which allows efficient lowering of the systems free energy by the formation of dopant clusters and pockets of liquid dopant. For metallic alloys, phase separation proceeds by spinodal decomposition described by the Cahn–Hilliard theory [33, 34, 35], where the origin of the new phase is non-nucleated demixing in the unstable regime. This is in contrast to nucleation and growth processes, which feature small and well defined points of origin, nuclei, of the new phase which grow in time. To investigate the process of dopant phase separation we simulate a static doped base crystal at $\mathbf{IF} = 0.03$. In this way the dopants can equilibrate throughout the matrix. After equilibration, when all the dopants have distributed themselves over the available tetrahedral sites, we allow the base particles to move as well; we switch the system from a rigid to a weak crystal. At this point we also start recording positional data both of the base and dopant particles. Using this approach we can study the early kinetics of dopant droplet formation (Fig. 3.9D). The process of phase separation is visible in the radial distribution function, $g(r)$, which we calculate for the dopants in the system. At $t = 0$ we find no structural peaks and the $g(r)$ resembles that of a gas indicating that our dopants form a solid solution. As time goes on we observe the appearance of structure peaks, including a shallow dip resulting from the finite size of the forming dopant droplets (Fig. 3.9C). Next we study the formed clusters in more detail.

Figure 3.9 – (A) Time evolution of the number of non clustered interstitial dopants, n_s . The solid lines are fits with stretched exponential functions, both with $\beta = 0.5$ — Standard Kohlrausch decay function (red) and the modified Kohlrausch function (blue). (B) The change of the number of dopant clusters, N_C (blue curve), and average cluster size, S_C (red curve), with time. (C) Radial distribution functions, $g(r)$, calculated for (from bottom to top) $t = 0, 0.125, 1.25, 3.13, 12.5, 62.5, 125, 188, 375, \& 994 \tau_B$.

We find that during the first stages a lot of small clusters are formed which grow by the addition of single particles still present as a solid solution. This is illustrated by the appearance of a high number of clusters whose size is small (Fig. 3.9B $t/\tau_B < 5$). Growth of the clusters on early timescales occurs by the addition of single dopants; the number of clusters stays constant during this time, while their size increases slightly (Fig. 3.9B $5 < t/\tau_B < 20$). On longer time scales, cluster–cluster combination events start to dominate — the number of clusters drops quickly while the average cluster size grows (Fig. 3.9B $t/\tau_B > 20$). These processes continue until the cluster number and their average size becomes stable. The different growth modes lead to a changing growth rate over time. We can capture this behaviour by looking at the decrease of non-clustered dopants as a function of time (Fig. 3.9A). The rate at which this clustering process takes place changes over time; early times are dominated by growth due to addition of single dopants to existing clusters, while at later times the clusters grow due to merger events between clusters. Because of the changing rate constant we can not fit this curve with a simple exponential decay, instead we fit it with a stretched-exponential decay function (Kohlrausch function) with a time-dependant rate constant of the form, $n_s(t) = n_{s,0} \exp(-k(t) \cdot t)$, with $n_s(t)$ the number of non-clustered dopants over time, $n_{s,0}$ the number of single dopants

at $t = 0$, and $k(t)$ the rate constant of cluster growth which can be expressed as $k(t) = \frac{\beta}{\tau_0} \left(\frac{t}{\tau_0}\right)^{\beta-1}$, with β , the stretching exponent, equal to $\frac{1}{2}$, and $\tau_0 = 1.75 \tau_B$ (Fig. 3.9A red solid line). This functional form captures the observed slowing down of cluster growth due to the transition from the addition of free dopants to the growth by cluster merger events. However, it assumes that the point where the kinetics go from faster-than-exponential to sub-exponential is at $t = \tau_0$ and it has the problem that at $t = 0$ the rate constant is infinite. In our case it is not a certainty that the transition point lies at the exponential lifetime τ_0 ; therefore we also try to fit an adjusted Kohlrausch function which has a rate constant that is always finite and decouples the transition point, t_0 , from the exponential lifetime, τ_0 . It has the form $k(t) = \frac{\beta}{\tau_0} \left(\alpha + \frac{t}{\tau_0}\right)^{\beta-1}$ [36], where $\alpha = t_0/\tau_0$. This function describes our data well and captures the exponential decay rate at short times (Fig. 3.9A top blue solid line) for $\tau_0 = 1.74 \tau_B$, and $\alpha = 0.051$. The small value of α confirms that, indeed, the first growth phase — single particle addition events — is very short compared to the later merger growth mechanism. The fact that a stretched exponential curve is required to describe cluster growth kinetics, implies that a distribution of characteristic reaction rates must exist. This is attributed to the cluster growth mechanism, which includes singlet addition to make a cluster grow with one dopant at a time, but also the simultaneous cluster growth through cluster-cluster merger. If we presume the rate constant to be diffusion-limited, the reactivity of a distribution of species with different sizes, will inevitably result in a distribution in reaction rate constants, hence the stretched-exponential shape we observe is the result of a continuous sum of exponential decays [37].

Conclusion

Doped weak bcc crystals of charged colloids exhibit a complex phase diagram in which we identify several transitions. At low levels of doping the dopants behave as an interstitial solid solution, occupying the tetrahedral interstitial sites of the bcc matrix. In the case of a rigid base crystal this is effectively the same behaviour as has been observed for colloidal binary systems with hard sphere matrices, where dopants diffuse through the lattice, hopping between interstitial sites. However, in our system, where fluctuations of the matrix lattice are substantial, we observe anomalous behaviour. The weak matrix allows for free movement of dopants — no longer bound by well defined minima in the potential energy field. On

top of that, the introduction of dopants with long ranged repulsive interactions into the crystalline matrix results in a finite lattice strain, even though particles are far apart. The ability of dopants to diffuse efficiently through our system allows the system to efficiently lower its free energy by separating the dopants out from the bcc matrix; this lowers the finite lattice strain due to the presence of dopants. It is the lowering of the lattice strain that drives the formation of dopant clusters and, at higher dopant concentrations, pockets of pure dopant liquid. The separation of dopants at supersaturated levels is also observed in doped metals such as carbon in α -Fe [6], with the distinction that in the case of Fe the carbon precipitates in the form of Fe_3C , whereas we form pure dopant phases. There also appears to be a preference for certain crystal planes to start forming carbon clusters before full precipitation [5]. We have not been able to observe any preference of this kind.

At even higher dopant concentration the finite-sized pockets merge and transition into one single dopant phase fully separated from the matrix, a crystal-liquid coexistence. Further increases in doping levels continuously increases the volume fraction of the dopant phase, which at some point crosses its freezing point. Even though volume fractions are higher than the freezing point, the observation of crystalline structure in the dopant phase is rare.

Our simulations are the in-silico model of the colloidal system with long-ranged Yukawa interactions made up of poly(methyl methacrylate) (PMMA) colloids [38, 39]. This opens up the exciting possibility of studying the phase separation of binary colloidal systems in experiments using the highly charged Wigner crystal systems. By contrast, in hard sphere systems, kinetically-trapped configuration are more likely to appear; it remains unclear for hard spheres if demixing in polydisperse systems can occur on experimentally realistic time scales for the volume fractions required to induce freezing [40, 41].

Finally, we note that so far we have studied the structure and ensemble-averaged phase behaviour of these anomalous doped crystals. Since their dynamical properties, such as their vibrational density of states and mechanics, are also of relevance for the practical use of doped materials with a bcc symmetry, understanding how large thermal fluctuations and the resulting non-affinity at the particle scale affect their dynamics is most certainly of interest for future study. For example, it has been established that small amounts of defects in well-ordered solids can lead to the emergence of a Boson peak in the density of states, which is typically a feature associated with amorphous solids [42, 32]. While it has recently been established that pure bcc crystals exhibit such anomalies [19], it remains unclear what effect doping may have. For the future, it will be interesting to explore if these effects also emerge not due to structural defects but due to the addition of interstitial dopants in these bcc phases,

as a means to manipulate their electronic and mechanical behaviour.

Methods

Simulations

We use Brownian Dynamics simulations, following the over-damped Langevin equation:

$$\frac{d\vec{r}_i}{dt} = \frac{1}{\gamma} [\vec{F}_{U,i} + \vec{\xi}_i] \quad (3.1)$$

where γ is the particle drag coefficient, $\vec{F}_{U,i}$ is the force acting on particle i resulting from all potentials and $\vec{\xi}_i$ is a random force with an average of zero, $\langle \vec{\xi}_i \rangle = 0$, and a mean squared value, $\langle |\vec{\xi}_i|^2 \rangle = 6k_B T \gamma / \delta t$. The equation of motion is integrated using the HOOMD-Blue software package, which uses the integration described first by Snook[43], drawing the random force term from a uniform distribution.

We perform the simulations on NVIDIA GeForce GTX 960 GPUs in single precision mode using the simulation package HOOMD-Blue version 2.0.3-7[44, 45].

Our simulation parameters are based on an experimental colloidal system of charged PMMA colloids interacting via long-ranged repulsive interactions [39, 19]. We use particle diameters of $\sigma_b = 1.8 \mu\text{m}$ and $\sigma_d = 0.9 \mu\text{m}$ for the base crystal particles and dopants respectively. We normalise all distances with respect to σ_b such that $\sigma_b = 1$. The chosen particle sizes on the order of a micron make sure that our simulation system is accessible in experiments and the size ratio of $\sigma_d/\sigma_b = 0.5$ is close to that of carbon dopants in iron.

The particles in our simulations all interact via a pair-wise repulsive Yukawa potential. It has been shown that this potential can capture the overall behaviour of experimental crystalline systems of these charged colloids [46]. We use a Yukawa potential of the form $U(r)/k_B T = \epsilon \frac{\exp(-\kappa r)}{r}$ for $r < r_{cut}$ and $U(r)/k_B T = 0$ for $r \geq r_{cut}$, where $r_{cut} = 10 \sigma_b$. We use the same parameters as we used in our previous simulation work [23] which have been mapped onto the experimental system's phase behaviour: $\kappa = 1.8 \sigma_b$, and $\epsilon_{b,b} = 713$; assuming a constant surface charge density we arrive at $\epsilon_{d,d} = 227$. We set $\epsilon_{d,b} = 470$ for the cross interaction by taking the average of the homo-interactions.

We simulate with a time step of $2.5 \cdot 10^{-5} \tau_B$, with τ_B the self diffusion time of the base particles in an infinitely diluted system calculated as $\tau_B = \frac{\sigma_b^2}{D_0}$, with $D_0 = \frac{k_B T}{6\pi\eta(\sigma/2)}$. We equilibrate the system for $10 \cdot 10^6$

steps ($2.5 \cdot 10^2 \tau_B$) followed by a further $90 \cdot 10^6$ steps ($2.25 \cdot 10^3 \tau_B$) during which we save dataframes every 500 steps.

Our primary simulations consist of 31,718 base particles, N_b , with a variable amount of dopant particles, N_d . We arrange the base particles on a perfect bcc lattice at a constant volume fraction $\phi_{base} = 0.1$ and place the dopant particles in tetrahedral interstitial sites of said lattice before starting the simulations. We express the number of added dopant particles as the fraction of filled tetrahedral interstitial sites, $\mathbf{IF}$, in the base bcc lattice — we simulate $\mathbf{IF} = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27 \& 0.30$. These correspond to $N_d = 738, 1477, 2216, 2954, 3693, 5540, 7387, 9234, 11080, 12927, 14774, 18468, 19945 \& 22161$. To find the melting point in a system consisting purely of dopant particles we generate a simulation box half-filled with a bcc lattice and half with randomised particle positions. We run these simulations for $10 \cdot 10^6$ steps. We also simulate the formation of clusters in time by starting with a static bcc lattice with 20 percent of tetrahedral interstitial sites filled with dopants. We let the dopants relax for $10 \cdot 10^6$ steps and follow this with $90 \cdot 10^6$ steps during which we allow the base crystal to move as well; every 500 frames we save positional data.

Data analysis

All data analysis is performed using Python in IPython (Jupyter) notebooks [47]; making use of the packages numpy, scipy, scikit-learn, and matplotlib [48, 49, 50, 51]. For the identification of dopant clusters we use the DBSCAN algorithm as implemented in scikit-learn with the maximum allowable neighbourhood radius, ϵ , equal to the average neighbour distance — the first minimum in $g(r)$ for each respective sample — and a minimal cluster size of 3 particles.

Calculation of bond order parameters

For the calculations of bond-orientational order parameters we call the BondOrderAnalysis program of Lechner [31]. This open-source software tool calculates three-dimensional orientational bond-order parameters based on spherical harmonics according to:

$$\bar{q}_l(i) = \sqrt{\frac{4\pi}{2l+1} \sum_{m=-l}^l \left| \frac{1}{\tilde{N}_b(i)} \sum_{j=0}^{\tilde{N}_b(i)} q_{lm}(j) \right|^2} \quad (3.2)$$

for $l = 6$ and where $\tilde{N}_b(i)$ is the number of neighbours of particle i and particle i itself, and $q_{lm}(k)$ is defined as the Steinhardt bond-order para-

meter [52]:

$$q_{lm}(j) = \frac{1}{N_b(j)} \sum_{k=1}^{N_b(j)} Y_{lm}(\mathbf{r}_{jk}) \quad (3.3)$$

, here $N_b(i)$ is the number of neighbours of particle j , and $Y_{lm}(\mathbf{r}_{jk})$ is the Laplace's spherical harmonic of the vector between particle j and particle k .

Calculation of ϕ_L

For the calculation of the local volume fraction, ϕ_L , of the dopant phases we employ Voronoi tessellation. For which we call out to the voro++ program [53]. The local volume fraction is defined as the ratio of the particle volume and the volume of its three-dimensional Voronoi cell, and subsequently ensemble-averaged:

$$\phi_L = \frac{1}{N_p} \sum_{i=1}^{N_p} \left[\frac{\frac{4}{3}\pi r_i^3}{V_i} \right] \quad (3.4)$$

where N_p is the number of particles in the population of interest, and r_i and V_i are the radius and volume of the enclosing Voronoi cell respectively of particle i .

Appendix

Radial distribution function — $g(r)$

In order to analyse the static structure of our samples we calculate the radial distribution function, $g(r)$, for every IF and separately for the base particles (Fig. A3.1A) and dopant particles (Fig. A3.1B).

Bond order parameter distributions — $P(\bar{q}_6)$ & $P(\bar{q}_4)$

For the two particle populations separately we calculate the bond orientational order parameter, $\bar{q}_6$ and $\bar{q}_4$, for every particle in the system. For the calculations we use the open-source BondOrderAnalysis [31] program and find nearest neighbours based on a cutoff distance r_{cut} equal to the first minima in $g(r)$ for each respective sample and particle type. We plot the probability distribution, $P(\bar{q}_6)$ and $P(\bar{q}_4)$, for the larger matrix particles (Fig. A3.2 and A3.4) and for the smaller dopant particles (Fig. A3.3 and A3.5).

Figure A3.1 – (A) Radial distribution function, $g(r)$, for base particles. Calculated for (bottom to top) $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$ & 0.30 . (B) Radial distribution function, $g(r)$, for dopant particles. Calculated for the same IF range as in (A)

Figure A3.2 – Probability distribution of the bond-orientational order parameter, $\bar{q}_6$ for base particles. Calculated for samples with (left to right; top to bottom) $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$ & 0.30 .

The distributions of the base particles show bcc crystalline symmetries over the entire IF range; as indicated by the peak around $\bar{q}_4 = 0.4$ and $\bar{q}_4 = 0.05$. This peak broadens in the IF regime ($0.01 < IF < 0.10$) where there is a coexistence of dopant droplets suspended in a bcc matrix, and sharpens again when full phase separation takes place ($IF > 0.10$).

The distributions of the dopant particles show broad distribution of $\bar{q}_6$ and $\bar{q}_4$ for $IF < 0.04$. This is because there are two populations of dopant particles; one which acts as interstitial dopants (peak around $\bar{q}_6 \geq 0.4$ and another where particles behave as a phase separated liquid ($\bar{q}_6 < 0.4$). For $0.04 < IF < 0.10$ the distribution is dominated by dopant liquid, until traces of crystallinity reappear at those IF values where the system is fully phase separated and the dopant phase has a volume fraction above its freezing point ($IF > 0.10$).

Figure A3.3 – Probability distribution of the bond-orientational order parameter, q_6 for dopant particles. Calculated for samples with (left to right; top to bottom) $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$ & 0.30 .

Interfacial enthalpy

In order to aid in the analysis of the stability of the clusters we calculate an interfacial enthalpy between the dopant and base phases, $\gamma_{b,d}$ term; similar to an interfacial energy, $\gamma_{b,d} \propto \frac{A_{b,d}}{U}$, where $A_{b,d}$ is the area between the dopant and base phases and U is the total potential energy of the system (Fig. A3.6).

Dopant droplet mean-squared displacement

Over the last $20 \tau_B$ of our simulation (for $IF=0.07$) we calculate the mean-squared displacement of entire dopant droplets by treating the centre-of-mass of each droplet as a particle and tracking its position over time. We observe rattling at short lag times which quickly turns into a plateau at longer lag times. This indicates that dopant droplets are immobile and appear kinetically trapped (Fig. A3.7).

Figure A3.7 – Mean-squared displacements for dopant droplets. Calculated over the last $20 \tau_B$ of our simulations for $IF = 0.07$.

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Figure A3.4 – Probability distribution of the bond-orientational order parameter, $\bar{q}_4$ for base particles. Calculated for samples with (left to right; top to bottom) $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$ & 0.30 .

Figure A3.5 – Probability distribution of the bond-orientational order parameter, $\bar{q}_4$ for dopant particles. Calculated for samples with (left to right; top to bottom) $IF = 0.01, 0.02, 0.03, 0.04, 0.05, 0.07, 0.10, 0.125, 0.15, 0.175, 0.20, 0.25, 0.27$ & 0.30 .

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Figure A3.6 — Interfacial enthalpy between dopant and base particle phases. **(A)** Total potential energy of the system, $U/k_B T$. **(B)** Total interfacial area between dopant and base particles phases, in units σ^2 , where σ is the diameter of a base particle. **(C)** Plot of total potential energy versus interfacial area. The solid line is a linear fit which gives us the enthalpic interfacial energy, $\gamma_{d,b} \propto \frac{A_{b,d}}{U}$, where $A_{b,d}$ is the area of the interface and U is the systems total potential energy.

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LINKING SLOW DYNAMICS AND MICROSCOPIC CONNECTIVITY IN DENSE SUSPENSIONS OF CHARGED COLLOIDS

4

The quest to unravel the nature of the glass transition, where the viscosity of a liquid increases by many orders of magnitude, while its static structure remains largely unaffected, remains unresolved. While various structural and dynamical precursors to vitrification have been identified, a predictive and quantitative description of how subtle changes at the microscopic scale give rise to the steep growth in macroscopic viscosity is missing. It was recently proposed that the presence of long-lived bonded structures within the liquid may provide the long-sought connection between local structure and global dynamics. Here we directly observe and quantify the connectivity dynamics in liquids of charged colloids en-route to vitrification using three-dimensional confocal microscopy. We determine the dynamic structure from the real-space van Hove correlation function and from the particle trajectories, providing upper and lower bounds on connectivity dynamics. Based on these data, we extend Dyre's model for the glass transition to account for particle-level structural dynamics; this results in a microscopic expression for the slowing down of relaxations in the liquid that is in quantitative agreement with our experiments. These results indicate how vitrification may be understood as a dynamical connectivity transition with features that are strongly reminiscent of rigidity percolation scenarios.

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"Linking slow dynamics and microscopic connectivity in dense suspensions of charged colloids"

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Introduction

FOR fragile glasses, the super-exponential increase in viscosity with small changes in temperature is often described by the phenomenological Vogel–Fulcher–Tamman (VFT) relationship [1]. The VFT form holds for a wide variety of fragile glass formers, ranging from metallic [2, 3] and molecular glasses [4, 5] to those formed by polymer chains [6] or colloidal particles [7]. However, a microscopic interpretation of this universal observation remains elusive. Seminal frameworks for the glass transition, such as mode-coupling theory (MCT), accurately predict the mechanism with which particle motion becomes localised from the static structure alone [8], but cannot recover the VFT law for the viscosity or relaxation time. The case of charged particles interacting via long-ranged Coulombic potentials has been explored by MCT with a predicted vitrified phase as a result [9]. For several systems of charged colloids, a glassy phase, or Wigner glass, has been identified, including charged polystyrene particles [10] and highly charged clay platelets [11, 12, 13, 14, 15, 16, 17]. In all of these experiments, scattering methods have been used to probe the often complex ensemble-averaged sample dynamics. However, not much experimental data is available in these charged systems that resolve the structure and dynamics down to the single-particle level.

To understand and predict how structural relaxations slow down in colloidal suspension upon increasing the particle concentration, it has been suggested that the emergence of frequency-dependent rigidity must be taken into account. The presence of a finite shear modulus at low frequencies is predicted to underpin the slowing down of particle motion, and the concomitant increase in the apparent viscosity, also at finite temperature [18, 19]. This finite-frequency rigidity cannot be understood solely from snapshots of the static structure. Rather, rigidity emerges from long-lived bonds between neighbouring particles [20, 21], which are needed to suppress nonaffine motions characteristic of liquids. It was recently proposed that the same long-lived structures govern their thermodynamics such as their internal energy and specific heat [18]. This implies that long-lived bonded structures may play an important role in the liquid state. The hypothesised connection between such structures and the viscoelasticity of liquids has been verified indirectly, for example for metallic alloys and polymer melts [22, 23]. Interestingly, within this picture due to the mobility and continuous restructuring of the liquid structure, rigidity emerges only beyond a finite and critical frequency.

Within the approach of Frenkel, Trachenko and Brazhkin [18, 24], this implies a continuous crossover from the liquid to the solid state, in which only the characteristic time-scale at which rigidity emerges becomes larger and larger; an idea recently proven experimentally [25]. While detailed studies of structure and dynamics in glassy liquids at the atomic or molecular scale are possible with a variety of scattering methods [26, 27], which have revealed much of our current knowledge of glassy dynamics, these do not allow identification of bonds at the level of individual cages between single particles. This type of information is however accessible in colloidal suspensions visualised using confocal microscopy.

In colloidal liquids, where dynamical slowing down can be induced by changing the particle packing fraction, several micro-structural and dynamical features have been identified to emerge as the liquid relaxations slow down and the glassy state is approached. While colloidal systems can by no means mimic all of the richness in phenomena found in atomic and molecular glasses, some crucial features can be observed and studied in colloidal systems as a proxy for these phenomena at much smaller scales. These range from the emergence of spatiotemporally heterogeneous dynamics [28, 29, 30] with features of criticality [31], localised “soft” vibrational modes [32] to structural signs in the form of icosahedral order [33], topological clusters [34, 35] and persistent fractal structures that are proposed to percolate at the liquid–solid transition [36]. Nonetheless, a key question remains: Is there a direct and quantitative correlation between the microscopic dynamics of long-lived bonded structures and the slowing down of liquids en-route to kinetic arrest?

In this chapter, we study suspensions of charged colloidal particles using three-dimensional confocal microscopy to identify and evaluate the dynamics of long-lived structures in colloidal liquids. We specifically chose colloids interacting through long-ranged electrostatic repulsion as this pushes the liquid–solid transition to lower volume fractions. This has the important advantage that surface interactions, such as frictional contacts and the resulting jamming, which may appear in colloidal hard-spheres, can be avoided possibly resulting in a cleaner view on the effects of local geometry on the suspension dynamics. In this approach, we have direct access to local structural dynamics at the single particle level. We directly obtain the dynamic coordination number in these experiments from real-space analysis. Based on these experiments, we reformulate Dyre’s elastic model for liquid relaxations. To obtain a prediction for the global relaxation time, we use the dynamics of local coordination number as input to describe the finite-frequency shear modulus within the approach of marginal spring networks. This yields a theoretical model based on microscopic properties that is in agreement with the experimental data. These results indicate how structural bonding dynamics at the nearest-neighbour level govern the macroscopic viscosity of these

liquids of charged colloids.

Results

Figure 4.1 – (A) Pair interaction potential determined in the dilute limit ($\phi \approx 0.008$, symbols) and fitted to a Yukawa potential (line). (B) Pair correlation functions $g(r)$ for $\phi = 0.18, 0.28$ and 0.35 (top to bottom), horizontally offset for clarity. (C) Static coordination number $Z(\tau = 0)$ with a cut-off at the first neighbour distance r_1 , taken as the first maximum in $g(r)$ (triangles), as r_2 , the first minimum in $g(r)$ (circles). (D) Nearest-neighbour distance r_1 in $g(r)$ as a function of particle volume fraction (E) Pair correlation functions with a distance axis rescaled as $r\phi^{1/3}$, for $\phi = 0.35, 0.31, 0.28, 0.26, 0.22$, and 0.18 . (inset) Probability distribution of the bond-orientational order parameter $\bar{q}_6$ showing a liquid structure and the absence of crystallites for $\phi = 0.35, 0.31, 0.28, 0.26, 0.22$, and 0.18 .

We study colloidal particles of poly(methyl methacrylate), stabilised by polyhydroxystearic acid, suspended in a density and refractive index matching mixture of apolar solvents (see Appendix for synthetic details). To suppress crystallization we use a binary mixture of particles with radii $a_{\text{small}} = 710$ nm and $a_{\text{large}} = 975$ nm as determined from light scattering. This gives a size ratio $a_{\text{small}}/a_{\text{large}} = 0.7$, which is known to effectively suppress crystallization [37]. The addition of 10 mM of the surfactant AOT leads to charging of the particles; in the apolar solvent this results in long-ranged repulsive interactions [38, 39]. We image the particles in three dimensions and time using confocal fluorescence microscopy and determine their centre-of-mass positions with ~ 30 nm accuracy.

Inversion of the three-dimensional pair correlation function $g(r)$ can

be used to gain insight into the particle interactions in the suspension. We use this approach in two different ways: i) in dilute suspensions and using an inversion based on the hypernetted-chain closure approximation to remove many-body effects can yield the two-body pair interaction potential [40, 41], ii) in concentrated suspensions, simple inversion of the pair correlation function gives access to the potential-of-mean-force which probes the effective interactions between two particles in the presence of many others, which thus includes all many-body effects.

First, we start by determining the pair interactions by measuring the $g(r)$ of a dilute suspension at $\phi \approx 0.008$, and invert this using the hypernetted-chain closure approximation (see Appendix) to obtain the pair interaction potential (symbols in Fig. 4.1A). The experimental data are well-described by the Yukawa potential $U(r)/k_B T = \epsilon \frac{\exp(-\kappa\sigma(\frac{r}{\sigma}-1))}{r/\sigma}$ (solid line in Fig. 4.1A) with $\sigma = 1.66 \mu\text{m}$, $1/\kappa = 1.0 \mu\text{m}$ the Debye screening length and $\epsilon/k_B T = 30.5$ the potential at contact.

At higher volume fractions ϕ , the instantaneous pair correlation function $g(r, \tau = 0)$, from a three-dimensional static snapshot of the sample, displays a liquid-like structure (Fig. 4.1B). As the volume fraction of particles is increased, the entire correlation function shifts monotonically to smaller values of r . This is shown by the shift in the position of the first peak r_1 as $r_1 \propto \phi^{-1/3}$, indicative of isotropic compression of the structure (Fig. 4.1D). Indeed, plotting the $g(r)$ for all volume fractions as a function of the re-scaled parameter $r\phi^{1/3}$ places the positions of the structure peaks in the curve onto a single re-scaled length scale (Fig. 4.1E), suggesting a almost homogeneous compression of the liquid structure, with little changes in its local geometry. This is corroborated by the fact that the instantaneous average coordination number $Z(\tau = 0)$ from snapshots of the liquid structure is virtually independent of ϕ (Fig. 4.1C); both when counting neighbours within a distance equal to the first maximum in $g(r)$ at r_1 and the first minimum in $g(r)$ at r_2 . We note, as we will show below, that the shape of the peaks in $g(r)$, in particular the curvature of the peak at its maximum, are very weakly but systematically dependent on volume fraction, such that we cannot strictly speak of a full collapse of the $g(r)$ by re-scaling the distance axis.

While we observe almost no changes in the local structure upon increasing the particle volume fraction, we find strong changes in particle dynamics across the same range of ϕ . We compute the intermediate scattering function $F_s(q, t)$ directly from our microscopy data as $F_s(q, t) = \langle \exp(i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]) \rangle$ where we choose $q = 2\pi/r_1$ as the scattering vector. We find two distinct decays in the dynamic structure factors (Fig. 4.2A); at long lag times a structural α -relaxation is observed, which is typically associated with cage breaking and structural relaxations. At short times, the particles explore the confines of their

Figure 4.2 – (A) Self-intermediate scattering function $F_s(q, t)$ at $q = 2\pi/r_1$ for (top to bottom) $\phi = 0.49, 0.35, 0.28, 0.31, 0.26, 0.22$, and 0.18 ; solid lines are fits to a double stretched exponential decay as explained in the text. (B) Relaxation times for α - (black circles), β -relaxation processes (blue triangles), as extracted from $F_s(q, t)$, and as determined from the decay of the dynamical coordination number, $Z(\tau)$ (green squares). Solid line is description for τ_α , from the reformulated theory of Dyre. Error bars represent the 95% confidence interval of the fit.

geometric cages, which results in a small β -decay at short times. These two processes are characterised by the relaxation times τ_α and τ_β , respectively; we extract these two characteristic time scales by fitting the experimental $F_s(q, t)$ to a double stretched exponential [7], $F_s(q, t) = A \exp[-(t/\tau_\beta)^\delta] + (1 - A) \exp[-(t/\tau_\alpha)^\gamma]$, with stretch exponents $\sim 0.5 - 0.9$.

We note that due to the inherent experimental constraints associated with particle-level imaging, the range of time scales that can be probed is limited. As a consequence, for the higher volume fractions the decay in $F_s(q, t)$ is only partially observed. We use these data nonetheless to extract a reasonable estimate for the structural relaxation time, but note that the accuracy of these values reduces as ϕ increases. Nonetheless, within experimental resolution we find a consistent trend in the growth of τ_α . For the highest volume fraction explored, we find no significant decay and hence this data set is not used for further analysis.

With increasing ϕ , the structural relaxation time grows as the liquid viscosity increases. At much larger volume fractions, $\phi > 0.40$, we see a time-independent plateau in $F_s(q, t)$ (black squares Fig. 4.2A), which indicates full dynamic arrest on experimental time scales. The β -relaxation time, extracted from $F_s(q, t)$ is virtually independent of ϕ and set by the

in-cage particle diffusion coefficient, whereas the structural α -relaxation time grows steeply over more than 4 decades (Fig. 4.2B). Following previous experimental studies of colloidal glasses [7, 42], we empirically identify the glass transition as the volume fraction where $\tau_\alpha/\tau_B = 10^5$, found at $\phi_g \approx 0.35$. We note that defining the exact point of vitrification along the different approaches that have been developed, such as mode-coupling theory [43], the random first-order transition approach [44] or the Adam–Gibbs theory [45], is not the focus of this chapter. Hence we use the empirical criterion used more frequently in experimental studies of colloidal systems.

By fitting the measured pair potential in the dilute limit (Fig. 4.1A) we have determined that the Debye screening length under dilute conditions is $\kappa^{-1} = 1.0 \mu\text{m}$. We can define an effective volume fraction, which takes the charge interactions into account, as $\phi_{\text{eff}} = \frac{4}{3}\pi(\bar{a} + \kappa^{-1})^3 n = (\bar{a} + \kappa^{-1})^3 \phi / \bar{a}^3$, with n the number density of particles and $\bar{a}$ the geometric mean of particle radii, as we work in a bidisperse system at a 1:1 number ratio. At the glass transition $\phi_g = 0.35$, the effective volume fraction is predicted to be $\phi_{\text{eff}} = 0.77$, which is well above where either vitrification or jamming is expected to occur. This suggests that self-screening of the interactions may be relevant at these particle concentrations.

The Debye screening length of an electrolyte solution is given by $\kappa^{-1} = \sqrt{\frac{\epsilon_r \epsilon_0 k_B T}{2 N_A e^2 I}}$ [46], in which, ϵ_r and ϵ_0 are the dielectric constant of the solvent and the dielectric permittivity of vacuum, respectively, N_A is Avogadro's constant, e the elementary charge and I the ionic strength in the solution. In a medium with very low ionic strength, addition of charged colloids introduces additional counterions which contribute to screening of their own interactions. If we naively assume a homogeneous ion distribution, the overall ionic strength $I = I_b + I_c$ can be decomposed into that of the background solvent I_b and the contribution due to counterions of the particles I_c . We express the latter as a function of the colloid valency z , particle size R and volume fraction ϕ as $I_c = \frac{3\phi z}{4\pi\bar{a}^3(1-\phi)N_A}$.

For our experimental system, the screening length of the background solvent at very low colloid concentrations is $\kappa^{-1} = 1.0 \mu\text{m}$. Knowing $\epsilon_r = 2.5$, we deduce that the effective ionic strength of the background equals $I_b \approx 3 \mu\text{M}$. For the PMMA colloids we use, in presence of the charging agent AOT, previous experiments have shown that the particle valence z is low but can vary substantially between different batches. For the sake of argument, and to arrive at a qualitative understanding of the potential relevance of self-screening, we choose $z = 100$ charges/particle, which was found to be a reasonable value for different batches by direct electrophoretic measurements [47]. At the glass transition $\phi_c \approx 0.35$, this naive approach predicts an increase in ionic strength due to counterions of $I_c \approx 40 \mu\text{M}$. As a consequence, the Debye screening length reduces to κ^{-1}

Figure 4.3 – Probability distribution of cluster sizes, $P(S_c)$, for the small particles **(A)** and the large particles **(B)** in our binary mixture, calculated for the sample with volume fraction $\phi = 0.18$. We find no clusters of any significant sizes for either particle species. **(A inset)** Probability distribution of the particle radii as identified by the locating algorithm; we use this to determine a rough cutoff radius (dashed line) by which we can identify the two different particle populations. For the cluster analysis we use the DBSCAN algorithm with parameter ϵ , the maximum allowable neighbourhood radius, equal to the first minimum distance in the pair-correlation function, $g(r)$, and a minimum cluster size of one. **(B inset)** Pair-correlation function, $g(r)$, for the two particle populations: large particles (blue triangles) and small particles (red circles).

$\approx 0.4 \mu\text{m}$, at which the effective colloid volume fraction becomes $\phi_{eff} = 0.52$, which is smaller than the glass transition predicted by MCT to occur at $\phi_g = 0.59$. The underestimation of the effective volume fraction is most likely due to ion correlations which will be significant in such under-screened systems. While an in-depth analysis would be required to detail these effects, this is not the purpose of this chapter, but this naive analysis at-least illustrates how non-trivial charge effects play a role. In our discussion we use the effective interactions from inversion of the pair correlation function to deal with these effects on a first-order phenomenological level.

The global dynamics could be influenced by local crystallinity or clustering of either particle species; as a check to make sure this is not the case we calculate the three dimensional bond-orientational order parameters, $\bar{q}_6$, for our system using the approach of Lechner et al. [48]. These data show a complete absence of any local crystalline structure, as indicated by the single peak around $\bar{q}_6 = 0.1$. (Fig. 4.1E inset) [48]. We are furthermore unable to find any ordered clusters of significant size for either particle species (Fig. 4.3).

We observe virtually no changes in the static coordination number,

from snapshots of the liquid structure, as a function of particle volume fraction, from the dilute liquid state to the kinetically arrested state at $\phi > \phi_g$. Over the same range of volume fractions, the particle diffusivity slows down by many orders-of-magnitude. This is a characteristic feature of the glass transition and highlights, as is the main challenge in understanding how the dynamical slowing down in liquids occurs, that the arrest of relaxations in the liquid cannot be explained from the static structure alone. It was recently proposed that the slowing down of relaxation processes in liquids upon decreasing temperature, or increasing density, may be understood by considering how visco-elasticity emerges at finite frequency due to the formation of persistent bonds between neighbouring particles [18, 22, 23]. This approach thus does not rely on the static structure, but rather takes the transient nature of neighbouring particle pairs into account, to evaluate their significance in contributing to the actual local rigidity of the structure.

This concept assumes that particles are capable of forming cohesive bonds. By contrast, our experimental system is composed of particles interacting with a purely repulsive pair potential (Fig. 4.1A), hence cohesion must be an emergent property caused by many-body correlations. These bonds can be defined as the presence of two particles in a close-enough proximity which enables them to carry a mechanical load, and thus contribute to the rigidity of the material. Despite the lack of cohesive forces, colloidal suspensions can develop a shear modulus [46] even when the interactions are purely repulsive, due to the formation of these effective ‘bonds’, or contacts which can carry a shear stress, when the suspension is contained at a finite fixed pressure.

Inversion of the pair-correlation function at finite volume fractions allows us to directly measure the potential-of-mean-force $w(r) = -\ln g(r)$ between the particles. These exhibit a clear bonding minimum at a distance that corresponds to the characteristic nearest-neighbour distance r_1 . This illustrates how, even in purely repulsive systems at a finite pressure, effective bonds emerge as a many-body effect.

These same emergent bonds allow repulsive colloidal systems to build up a finite elastic shear modulus, as demonstrated extensively in the literature [46]. The spring constant k that characterises the stiffness of these bonds, obtained by fitting the minimum in $w(r)$ to a harmonic well, increases slightly with increasing volume fraction; its absolute value of $k = 3.5\text{--}5.5 k_B T / \mu\text{m}^2$ is of order $k_B T / r_1^2$ as expected for a system governed by soft interactions (Fig. 4.4). We note that while the rescaling of $g(r)$ with $r\phi^{1/3}$ yields a collapse of the *position* of the curve, the width of the peaks narrows by a small amount as the volume fraction is increased, signifying a slight increase in the bond stiffness as expressed by the increase in k with ϕ .

To ascertain the dynamics of these bonds that emerge in liquids of re-

Figure 4.4 – The potential of mean force $w(r)$, determined from inversion of the $g(r)$ at finite volume fractions $\phi = 0.31$, 0.26 , and 0.18 . **Inset** Effective spring constant k of the particle-particle bonds, as determined from the curvature of $w(r)$.

Figure 4.5 – (A) Decay of the normalised coordination number $Z(t)/Z(0)$ as calculated from experimental particle trajectories, for different volume fractions (left to right) $\phi = 0.18, 0.22, 0.26, 0.35, 0.28$, and 0.31 . Solid lines are stretched exponential fits for the determination of τ_Z . (B) Typical decay time of $Z(\tau)/Z(0)$ as a function of neighbour cutoff distance r_c . Calculated from experimental trajectory data for $\phi = 0.31$. Solid red line is a power law fit with an exponent of two. (inset) Average coordination number Z at the Brownian timescale τ_B as a function of volume fraction. Calculated from the particle tracks (black solid triangles). Solid lines are power law fits to the data.

pulsive particles, we aim to extract the dynamical coordination number $Z(\tau)$ from our three-dimensional confocal microscopy data. This quantity probes how an initial set of nearest-neighbours exchanges as time progresses; while the average coordination number at any given snapshot may remain the same, particle motion will reshape the cages around a reference particle by breaking existing bonds and reforming new ones such that $Z(\tau)/Z(0) < 1$. We note that other metrics for probing the restructuring of confining cages exist, e.g. that proposed by Rabani et al. [49, 50, 51]; here we choose specifically to use $Z(t)$ which can be obtained directly from our particle-level experimental data without any arbitrary parameter choices and has been used successfully in the past to probe nearest-neighbour bond relaxation [52, 53, 36] and is thus established as a reliable metric.

We can determine $Z(\tau)$ directly from the three-dimensional particle trajectories, as was previously done for hard-sphere suspensions and attractive colloidal systems [36, 53, 21]. For every particle, at a given reference time, we identify its neighbours within a cut-off distance r_c , which we set equal to the first minimum in $g(r)$, at a lag time of $\tau = 0$ to find $Z(0)$. We then compute the time-trace of the separation distance

between a probe particle, i , and its neighbours, j , as a function of lag times, $d_{ij}(\tau) = |\mathbf{r}_i(\tau) - \mathbf{r}_j(\tau)|$. A neighbour exchange, and thus a loss of the original configuration of neighbours, is identified when $d \leq r_c$, for a given pair, allowing us to construct $Z(\tau)$. To ensure sufficient statistics we perform time- and ensemble averaging, yielding $Z(\tau)$ as shown in Figure 4.5A.

To test the effect of the length scale r_c on the erosion of a given bonding configuration, we determine the decay time τ_Z of $Z(\tau)/Z(0)$, by fitting $Z(\tau)/Z(0)$ with a stretched exponential, as a function of r_c , for $\phi = 0.31$ (symbols in Fig. 4.5B). We find $\tau_Z \propto r_c^2$ (solid line Fig. 4.5B), indicating the diffusive nature of neighbour exchange processes. The stretched exponential nature of these connectivity relaxations is related to the stretched exponential decay of self-relaxations as probed by the self-intermediate scattering function and hints at heterogeneous dynamics, well established to emerge in colloidal system upon approaching their glass transition point [28, 29].

We emphasise that the nearest-neighbour exchange dynamics probed by $Z(\tau)$ is a different measure for relaxations in the liquid than the self-mobility probed in $F_s(q, t)$, but rather is a collective (or distinct) effect. The dynamical coordination number probes how particles move with respect to its bonded neighbours. For example, the sliding of two particles with respect to each other, while remaining bonded, or the collective plug-like motion of a cluster of particles in a shear-transformation zone, does not lead to a reduction in Z but does lead to a decorrelation of $F_s(q, t)$. By contrast, cage rattling may break bonds such that $Z(\tau)$ decays while it results in only very weak decay in the dynamic structure factor. Indeed, the characteristic timescale for reconfiguration of a coordination shell τ_Z is lower and grows less steeply than τ_α obtained from fitting $F_s(q, t)$ (Fig. 4.2B).

Of special interest is the change in of $Z(\tau)$ as a function of ϕ as this provides a clue to the effect of local coordination dynamics on the volume fraction induced quenching of relaxation processes. At high frequencies, i.e. short τ , the scaling of Z with ϕ is weak, as both dilute and denser liquids have most of their original neighbours still in place (Fig. 4.5A). The differences between fast and slowly relaxing liquids become increasingly pronounced as the frequency is reduced, and concomitantly the steepness with which Z grows with ϕ increases.

So far we considered only the ensemble-average coordination number; however, a prototypical feature of liquids that slow down and approach their glass transition is that their dynamics become strongly heterogeneous [28, 29, 30]. To probe the spatial homogeneity of coordination structures, we reconstruct our experimental data by colour-coding particles according to their dynamical coordination number Z , taken both as the static structure $Z(\tau = 0)$, at the Brownian timescale

Figure 4.6 – Computer-generated renderings of our experimental system, in which the particles are colour-coded according to their actual coordination number: **(A)**: $Z(\tau = 0)$, **(B)**: $Z(\tau = \tau_B)$, and **(C)**: $Z(\tau = 250 \text{ s})$. Dark blue particles have $Z \geq Z_c$, while particles with $Z < 6$ are coloured in increasing shades of yellow, shown for $\phi = 0.3 \text{ l}$.

$Z(t = \tau_B \sim 10^1 \text{ s})$, and at long timescales $Z(\tau = 250 \text{ s})$. Indeed, we observe not only how the average coordination number at the Brownian timescale, $Z(t = \tau_B)$, decreases as the volume fraction is reduced (Fig. 4.7 middle row), but also how the distribution of coordination numbers is strongly heterogeneous in space (Fig. 4.6). From the reconstructions it is also clear that the debonding events through which the sample loses rigidity do not occur homogeneously throughout the sample; areas of high connectivity stay connected while areas with low connectivity weaken rapidly. Due to the heterogeneity of local coordination numbers, as observed in the reconstructed experimental data, the distribution of static coordination numbers $P(Z)$ for $\tau=0$ is broad. However on average it is constant as a function of volume fraction (top row in Fig. 4.7). As lag time increases and the liquid relaxes, $P(Z(\tau = \tau_B))$ shifts to lower values and narrows with volume fraction (middle row in Fig. 4.7). At long lag times, most of the original neighbours have translated away and the liquid has fully relaxed (bottom row in Fig. 4.7).

Discussion & Conclusion

We observe a marked increase in structural relaxation time over 4 orders-of-magnitude upon increasing ϕ during which the static coordination number $Z(0)$ remains virtually constant. This is a well-established feature of most glassy systems and implies that relaxation slowdown cannot be understood from considering static structures alone. It was recently proposed that, rather than using the static structure as a starting point

Figure 4.7 – Probability distribution of coordination numbers. For (left to right) $\phi = 0.31, 0.28, 0.26, 0.22$, and 0.18 we show the probability distribution of coordination numbers $P(Z)$. **top row**, Probability distributions of $Z(\tau = 0)$, the static coordination number; **middle row** Probability distributions of $Z(\tau = \tau_B)$. **bottom row** Probability distributions of $Z(\tau = 250 \text{ s})$.

to explain the dynamical slow down, one should consider those bonds which are sufficiently long-lived to contribute to rigidity at relevant frequencies [22], in other words, it is suggested that we need to consider the structural dynamics of those neighbours that share load-bearing bonds.

In order for local structure to contribute to rigidity, the cage that surrounds a central particle, needs to be intact for a least as long as the required time of escape. Bonds that break before the attempted escape from a cage, do not contribute to the slowing down of particle dynamics. The characteristic timescale of particle escape from a cage will be of the order of the Brownian time scale $\tau_B = a^2/D \sim 10^1 \text{ s}$, with D the particle self-diffusion coefficient. Thus, bonds which live longer than τ_B can contribute to a stable interconnected structure that provides the liquid with shear rigidity at Brownian frequencies. The concept that long-lived neighbours contribute to the formation of rigid structure in the liquid, revolves around the idea that the transition from a liquid-like to a solid-like response is signalled by the formation of an isostatic structure of load-bearing bonds at a characteristic frequency. Note that this is not the same as the zero-frequency liquid-solid transition, which is the focus of the jamming framework and which signals the arrest of flow on all timescales. Rather, the location of this frequency-dependent liquid-solid transition in these thermal fluids will depend on the choice of frequency [25]; for the purposes of this discussion we use the characteristic frequency $\omega_B = 1/\tau_B$.

From the experimental data for $Z(\tau)$, we can measure the value of the coordination number at $\tau = \tau_B$ as a proxy for the amount of bonds that could contribute to rigidity (inset Fig. 4.5B). We find that $Z(\tau_B)$ grows as the particle volume fraction is increased, whereas the static coordination

number $Z(\tau = 0)$ remains constant over the same range of volume fractions (Fig. 4.1C).

For the frequency of interest, ω_B , a liquid-solid transition must emerge at some critical volume fraction ϕ_c , where in accord with the Maxwell criterion for isostaticity in three-dimensional central-force lattices, $Z(\tau_B) = Z_c = 6$. To link the emergence of frequency-dependent elasticity to the slowing down of particle dynamics, we adopt the phenomenological model developed by Dyre. This approach treats relaxation events, occurring at finite frequency, as localised shear deformations of the surrounding medium; such local shear transformations have been observed experimentally in dense colloidal suspensions [54]. By combining thermally-activated dynamics of the Eyring type with continuum mechanics, Dyre analytically derived a relationship between the structural relaxation time and the shear modulus G of the liquid [55] as $\tau_\alpha = \tau_B \exp \left[\frac{GV_a}{k_B T} \right]$, where V_a is the activation volume. The term $E_a = GV_a$ represents the elastic activation energy to expand the cage allowing an irreversible rearrangement to take place. It is important to note that in Dyre's model, the local shear rigidity is described by the high-frequency shear modulus, which is close to predictions from affine elasticity.

A microscopic interpretation of the shear modulus is provided by the framework for disordered bead-spring lattices [56], which gives the affine shear modulus as [20]; $G = \frac{1}{5\pi} \frac{k(\phi)}{r_1(\phi)} \phi Z$, with k the effective spring constant of the interparticle bonds, which depends on ϕ (inset Fig. 3) and r_1 the average interparticle spacing. We note that this formulation unites the models of Dyre and Frenkel [55, 24], where the term GV_a is the density of elastic potential energy, since the spring constant is the curvature of the minimum in the potential of mean force, multiplied by the number of connections Z , divided by r_1 gives us the total potential energy density experienced by a particle within a parabolic approximation.

As discussed above, even though we work with repulsive colloidal particles, effective bonds emerge as a many-body phenomenon (Fig. 4.4) whose spring constant $k(\phi)$ grows and average interparticle distance r_1 shrinks slightly as ϕ increases (inset Fig. 4.4 & Fig. 4.1D).

We estimate the activation volume V_a as the cage volume $V_a = \frac{4}{3}\pi r_1(\phi)^3$. We now obtain a version of Dyre's elastic model in terms of particle-level quantities:

$$\tau_\alpha = \tau_B \exp \left[\frac{4k(\phi)r_1(\phi)^2 Z(\phi)\phi}{15k_B T} \right] \quad (4.1)$$

in which the microscopic parameters can be directly extracted from the experiments. To evaluate the local connectivity Z , we must realise that rigidity in the liquid state only emerges above a finite frequency

[18, 24]; this raises the question what the appropriate frequency is to evaluate Z . Within the picture of Frenkel [24], the characteristic frequency at which rigidity should be evaluated corresponds to the attempt frequency of particle escape from their cage. In our case, the characteristic attempt frequency $\omega_0 \propto 1/\tau_B$, such that we must take $Z(\tau_B)$ as the appropriate measure for local connectivity (inset Fig. 4.5B). If we presume that the dependence of $Z(\tau_B)$ with volume fraction obeys a scaling, $Z(\tau_B) = Z_c(\frac{\phi}{\phi_c})^b$, we can identify a solid-liquid transition point at ϕ_c . However, our experimental data does not span a large enough range of volume fractions to draw a rigorous conclusion if this power-law scaling is found. Thus, we assume it to hold, and find by comparing the limited amount of experimental data to this form, $b = 1.8$ and $\phi_c \sim 0.45$ (inset Fig. 4.5B). A true test of the validity of this rigidity collapse argument requires an in-depth study of the local structure with volume fraction e.g. by means of extensive computer simulations, which is beyond the scope of this chapter. This allows us to reformulate the equation in terms of directly observable quantities alone:

$$\tau_\alpha = \tau_B \exp \left[\frac{4k(\phi)r_1(\phi)^2 Z_c \phi^{1+b} \phi_c^{-b}}{15k_B T} \right] \quad (4.2)$$

This model provides a reasonable agreement with experimentally determined values for the relaxation time τ_α (solid line in Fig. 4.2B). We note that this is a model based only on directly observable microstructural properties, which gives a predictive connection between the liquid structure and the emergence of rigidity at finite frequency. Thus, this form reconciles the approaches of Dyre and Frenkel [55, 24].

The agreement between experimental data and this theory illustrates how liquid viscosity at the global scale could possibly be understood from the existence and dynamics of long-lived, or persistent, emerging bonds between neighbouring particles. This may also imply that the slowing down of liquid relaxation processes, in analogy to those in metallic alloy melts or polymer fluids [22, 23], is a dynamical connectivity transition leading to the isostatic condition at a finite, relevant, frequency. This conclusion is in direct agreement with the conceptual picture of fluidity and rigidity first proposed by Frenkel [24], and expanded on by Trachenko and Brazhkin [18], in which vitrification is a continuous transition in which the characteristic frequency at which rigidity emerges shrinks as the solid state is approached. The emergence of rigidity in liquids far away from any macroscopic phase transition was recently evidenced also for molecular systems, further supporting our claims [25]. A more complete understanding of the link between connectivity and the slowing down of relaxation processes, and its relation to the glass transition, requires a more detailed theoretical analysis of the problem, in which the

frequency-dependence is treated explicitly and the spatial inhomogeneity and heterogeneous dynamics are taken into account [57].

Methods

As an experimental model for charged colloids in apolar media, we use spherical particles, composed of poly(methyl methacrylate), stabilised by a comb-polymer of polyhydroxystearic acid grafts on a PMMA backbone at their surface. For details on the synthesis and characterisation we refer to the SI. We use particles with radii $a_{small} = 710$ nm and $a_{large} = 975$ nm as determined by static light scattering, in a 1:1 ratio by volume. The particles are suspended in a density-matching mixture of *cis*-decalin and tetrachloroethylene containing 10 mM Aerosol OT as a charging agent [38]. Density matching conditions are established by adjusting the solvent mixture until we observe no visible sedimentation after centrifugation at 2000 g for 1 hour. This solvent mixture also has a similar refractive index to the particles, ensuring optical transparency and minimising scattering, thus enabling observation deep into the sample with confocal microscopy. We load the suspension into glass sample chambers (extended description of sample chamber construction in Appendix), hermetically sealed using Norland Optical Adhesive. We image the samples using confocal fluorescence microscopy using a VT-Infinity3 confocal module from VisiTech International, mounted on a Nikon Ti-U inverted microscope. Images are captured with a Hamamatsu sCMOS ORCA-Flash4.0 camera. For most analysis we use three-dimensional image stacks recorded in time; we capture 2500 three-dimensional xyz-image stacks at 2 Hz, with a field of view of $205 \times 205 \times 75$ voxels (voxel volume $0.25 \times 0.25 \times 0.33 \mu\text{m}^3$). For the analysis of sample dynamics using the intermediate scattering function $F_s(\mathbf{q}, t)$ we require a higher time resolution; to this end we record 30,000 two-dimensional slices through our three-dimensional system at a frequency of 20 Hz. From the raw confocal images we extract the particle centroid positions with subpixel resolution using established algorithms both for two- and three-dimensional data [58], and link these together into particle trajectories. Recent advances in particle locating have lead to the development of locating algorithms which improve some weaknesses in the standard algorithms, in particular for suspensions in which the interparticle distance becomes comparable to the particle diameter, by means of iterative locating [59]. We have compared our data with results on the same data sets using these iterative algorithms and find no difference. Thus, in our case, the use of these enhanced algorithms does not lead to improvement

in data. Due to the charges on the particle surface, the interparticle separation never approaches the particle diameter, such that the tracking accuracy is not enhanced by iterative routines. All other data analysis is performed using dedicated *MATLAB* scripts, which are available upon request from the authors.

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Appendix

Synthesis

All materials are purchased from Sigma–Aldrich (SA) and used as received, unless specified otherwise. For the synthesis of poly(methyl methacrylate) (PMMA) colloidal particles we use: methyl methacrylate (MMA, SA M55909), methacrylic acid (MA, SA 155721), hexane (SA 208752), mineral oil BioUltra (SA 69794), 2,2'-Azobis(2-methyl-propionitrile) (AIBN, SA 441090), 1-octanethiol (SA 471836), and 3,3'-dioctadecyloxacarbocyanine perchlorate (DiO, ThermoFischer Scientific D-275). For the synthesis of poly(12-hydroxystearic acid)-*graft*-poly(methyl methacrylate) (PHSA-g-PMMA) we use: 12-hydroxystearic acid (TCI Chemicals, H0308), toluene (SA, 179965), methanesulfonic acid (SA 471356), 4-*tert*-butylcatechol (SA 124249), glycidyl methacrylate (GMA, SA 151238), N,N-dimethyldodecylamine (SA 284386), ethyl acetate (SA 16371), and butyl acetate (SA 537454). We also use *cis*-decahydronaphthalene (cDec, TCI Chemicals D0009), tetrachloroethylene (TCE, SA 270393), and docusate sodium salt (AOT, SA 86140).

Synthesis of poly(12-hydroxystearic acid)-*graft*-poly(methyl methacrylate)

Our synthetic procedure for poly(methyl methacrylate)-*graft*-poly(12-hydroxystearic acid) (PMMA-g-PHSA), the stabiliser used in the synthesis of colloidal PMMA particles, follows the general three-step procedure as detailed in literature [60], with some minor changes.

Step I - We begin by creating oligomers of 12-Hydroxystearic acid (HSA), aiming for oligomers of around 5 monomers in length, using a polycondensation reaction. To this end we weigh 50 g HSA and 9 g toluene in a 500 mL two necked round-bottom flask equipped with a reflux condenser and a 15 mL Dean–Stark trap, with 12 mL of toluene added to receiver leg. We heat the setup via an oil bath set at 110 °C and wait for the HSA to fully melt and dissolve in the toluene, while vigorously stirring the solution. After the HSA has fully dissolved we add 0.11 g of methanesulfonic acid and set the temperature of the oil bath to 150 °C. We let the reaction reflux for 20 hours, during which the reaction goes from a very pale yellow to a dark brown in colour and the viscosity of the solution increases strongly. During the condensation reaction a total of ~1.5 mL of water are extracted from the flask into the Dean–Stark trap.

Step II - After 20 hours we empty the receiver leg of the Dean–Stark trap and add 20 mL of toluene to the reaction. We azeotropically distill 15 mL of the added toluene to remove all condensation water from the reaction. We then react the terminal carboxylic group on the PHSA with glycidyl methacrylate (GMA), to create reactive PHSA macromonomers. In a separate beaker we combine 5.2 g GMA, 0.073 g *tert*-Butylcatechol, 0.20 g *N,N*-Dimethyldodecylamine, and 10 g toluene. We add this solution to the refluxing reaction and allow it to react for another 7 hours while stirring vigorously. At completion the reaction is cooled and stored at 4 °C until further use.

Step III - In the third step we co-polymerize MMA and the PHSA macromonomer, to create the PMMA-*graft*-PHSA stabiliser. We prepare a mixture of 31 g PHSA macromonomer, as synthesised in steps I & II, 9.2 g toluene, 18.32 g methyl methacrylate, 2.05 g glycidyl methacrylate, and 0.307 g AIBN. We slowly add this mixture dropwise, using a syringe pump, over a period of three hours to a round-bottom flask equipped with a reflux condenser, containing 13.94 g ethyl acetate and 6.97 g butyl acetate which is immersed in a 110 °C oil bath. After the reaction mixture has been added to the flask we let the reaction proceed under reflux for two hours after which we add a solution of 140 mg AIBN in 1.5 g ethyl acetate and 0.75 g butyl acetate. When another two hours have elapsed we add another dose of AIBN. After addition of the second injection of AIBN we dilute the reaction with 16.6 g ethyl acetate and 8.3 g butyl acetate. We let the reaction proceed for 15 hours. After cooling to room temperature, the stabiliser reaction mixture is used directly in the synthesis of the particles. The resulting product is highly viscous and has a golden colour.

Synthesis of PMMA colloidal particles

For the synthesis of colloidal particles made out of poly(methyl methacrylate) (PMMA) [61] we add 49.0 g Methyl methacrylate (98% of total

Figure A4.1 – Size determination of colloidal particles with SLS.

(A) Rayleigh ratio as a function of scattering vector for the smaller particles q , solid red line is a theoretical fit as calculated using Mie theory giving a radius of gyration of 710 nm (black circles). (B) Same as in (A) but for particles with a radius of gyration of 975 nm.

monomer weight), 1.0 g Methacrylic acid (2% of total monomer weight), 29.8 g Hexane, 14.3 g Mineral Oil, and approximately 10 mg of DiO-C18 fluorescent dye to a 250 mL round-bottom flask. We add a small magnetic stirring bar and stir the solution until all the dye has dissolved. We then add 5 g of PMMA-g-PHSA stabiliser, 390 mg AIBN, and 300 mg 1-Octanethiol. The reaction takes place under reflux conditions at 80 °C and proceeds for 2 hours under slow magnetic stirring. We then filter the reaction mix through glass wool. Reaction products are removed by cleaning the suspension through centrifugation against hexane (2 ×). The resulting particles have a radius of 710 nm as measured by static light scattering (Fig. A4.1A). By increasing the amount of monomer used, the particle size can be increased. Using this method we synthesise a second batch of particles with a radius of 975 nm as determined by SLS (Fig. A4.1B).

Sample preparation

Washing and density matching of particle suspension - We start by washing, by sequential centrifugation and re-suspension steps, the particle suspensions two times with a 50/50 volume-% mix of *cis*-Decahydronaphthalene (cDec) and Tetrachloroethylene (TCE) with 10 mM AOT. By varying the relative volumes of cDec and TCE we can density match our particles with the solvent mix. We achieve this by adding small amounts of TCE or cDec until we can no longer observe sedimentation after centrifugation at 2000 g for one hour. The density matched suspension is also matched well enough in refractive index to allow us to examine the samples using confocal microscopy up to depths of approximately 100 μm , without loss of resolution due to scattering. After density matching the particle suspensions we concentrate the suspension by centrifuging at 2500 g and

35 °C until we observe a clear supernatant. We decant the supernatant and store it for later use. All subsequent samples are made from this concentrated stock suspension and are diluted with the supernatant.

Figure A4.2 – Side view of the sample chambers used in this study. The shaded blue area represents the hollow where the sample is loaded.

Sample chamber fabrication - Our sample chambers are constructed by gluing, using Norland Optical Adhesive 61 UV curable glue, two 21 mm × 26 mm microscopy cover slips on a larger round cover slip (radius of 2.5 cm); leaving a space between them of approximately 0.5 cm. We then glue a microscope slide (26 mm × 76 mm) across the two rectangular cover slips using the same UV glue. This creates a hollow chamber with dimension of approximately 5 mm × 26 mm × 150 μm. The sample chamber construct is depicted as a side-view in Figure A4.2 with the loaded sample shaded in blue. We load the sample chambers using capillary forces and seal both ends of the chamber with 2-component gel epoxy from VersaChem.

Pair potential $U(r)$

The pair potentials $U(r)$ is obtained from the measured radial distribution function $g(r)$ using the Ornstein-Zernike relation:

$$h(r) = c(r) + \rho \int h(r')c(r-r')d\mathbf{r}' \quad (4.3)$$

where $h(r) = g(r) - 1$ is the total correlation function, $c(r)$ the direct correlation function, and ρ the number density of particles. We solve this equation by Fourier transformation, using the hypernetted chain (HNC) closure approximation:

$$c(r) = -U(r)/k_B T + h(r) - \ln g(r) \quad (4.4)$$

This closure approximation is known to give accurate results for soft potentials at not too high densities [40].

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VALIDITY OF THE VINEYARD APPROXIMATION IN COLLOIDAL WIGNER GLASSES

5

The glass transition in colloidal Wigner systems can be successfully described as a dynamical connectivity transition. The central parameter in the dynamical transition is the dynamical coordination number, $Z(\tau)/Z_0$, which describes the reshaping of the bond structure that gives the system rigidity. While this quantity is readily accessible from single-particle level experiments on colloids, there is no method to measure it using scattering methods. In this chapter we show how the Vineyard approximation can be used to directly gain the dynamical coordination number from the intermediate scattering function, $F(\mathbf{q}, t)$, which is accessible via scattering methods. However, the validity of this approximation remains unconfirmed for dense liquids close to vitrification. We show that the Vineyard approximation is valid, up to the point of dynamical arrest. This method opens up possibilities to test the idea of dynamical connectivity in atomic or molecular systems for which we do not have access to data at the level of single atoms or molecules.

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Introduction

In the previous chapter we treated the colloidal glass transition through the eyes of liquid theory [1, 2]. We showed that the colloidal glass transition is governed by the dynamical connectivity of the system. Each particle has a constant number of force-bearing neighbouring particles, Z , at any point in time, but the dynamical evolution of these emergent bonds, $Z(\tau)$, dictate the time-dependence of the liquid rigidity and thus controls whether the system responds as a liquid or a solid at the relevant frequency. It is the long-lived, or persistent, bonds which contribute to the solidity of the system.

We interpret the glass transition as a transition in dynamical connectivity, that is to say: there exists a finite, relevant, frequency at which long-lived bonds satisfy the Maxwell isostaticity condition and give the system rigidity. In the case of soft colloids we took this relevant frequency, ω , to be the attempt frequency of colloids escaping from their cage, approximately $\omega_B \approx \tau_B^{-1} \approx 10^{-1}$ Hz; as particles continuously exchange positions only bonds which live longer than τ_B can contribute to a stable interconnected structure that provides the liquid with rigidity.

To test our hypothesis that the glass transition is governed by the bond connectivity network we extracted the absolute number of neighbours at the Brownian time, $Z(\tau = \tau_B)$ from $Z(\tau)$ and used its dependence on volume fraction, ϕ , to make a prediction for the relaxation time-scales as a function of ϕ . This prediction successfully links local structural dynamics to the global dynamical arrest as a system approaches the glass transition. In this way we have shown that the glass transition, in systems of charged colloids with long ranged-repulsion, is a dynamical connectivity transition. These systems are often described as ‘Wigner systems’ in analogy with highly correlated electron crystals as found on semiconducting hetero-surfaces and on the surface of liquid Helium [3].

The central parameter in our prediction is $Z(\tau)$, which we get directly from single-particle level experiments. While for a colloidal system studied with confocal microscopy it is trivial to calculate $Z(\tau)$ simply by counting particles, this quantity is not easily accessible in atomic or molecular glasses. To test our theory in those systems we need a method to access $Z(\tau)$ from data obtained by scattering methods.

The full dynamical behaviour of a system is captured in the van Hove function, $G(r, t)$ or its Fourier transform, the intermediate scattering function $F(\mathbf{q}, t)$. Both functions consist of a self and a distinct part that describe the dynamics of a single particle or the correlated dynamics with

other particles in the system, respectively. The dynamical connectivity, $Z(\tau)$, of a system is encoded in the time-dependence of the distinct part. It is the distinct part that captures the cross-correlation in dynamics between different particles: the dynamical connectivity. The full intermediate scattering function, $F(\mathbf{q}, t)$ is easily accessible from scattering experiments. However, splitting the function into the self and distinct part is not trivial.

One method to make this split is the Vineyard approximation. This method expresses the full intermediate scattering function $F(\mathbf{q}, t)$ as the convolution of the static structure factor $S(\mathbf{q})$ with the self-part of the intermediate scattering function $F_s(\mathbf{q}, t)$: $F(\mathbf{q}, t) \simeq S(\mathbf{q})F_s(\mathbf{q}, t)$ (see Appendix). With this approximation we can describe $F_d(\mathbf{q}, t)$ in terms of the full intermediate scattering function and the static structure factor. Once we know $F_d(\mathbf{q}, t)$ we get to $G_d(r, t)$ via a spatial reverse-Fourier transform.

While the Vineyard approximation has been tested for simple liquids [4, 5], it remains untested for liquids close to the glass transition. In this chapter we set out to prove or disprove its applicability in such a system. If the Vineyard approximation holds in near-glassy liquids the long-time behaviour of the intermediate scattering function and the dynamical coordination number should follow identical scaling. We calculate both quantities from our experimental confocal data and indeed find a match within experimental error. This finding implies that the Vineyard approximation holds for Wigner liquids approaching the glass transition and opens up the possibility to test our prediction on atomic and molecular systems.

Methods

The experimental methods used in this chapter are the same as those used in chapter 4. In brief: our experimental system consists of charged colloidal particles of poly(methyl methacrylate), stabilised by polyhydroxystearic acid (PHSA), suspended in a density and refractive index matching mixture of *cis*-decaline and cyclohexylbromide. We use a binary mixture of particles with size ratio, $a_S/a_L = 0.7$, where a_S and a_L are the radii of the small and large particles respectively. This mixture is known to be an effective glass former [6]. To induce charging of the particles, we add 10 mM of the surfactant dioctyl sulfosuccinate sodium salt (AOT), which results in this low dielectric solvent in long-ranged repulsive interactions of the screened Coulomb type[7, 8].

We image the particles in three-dimensions and time using confocal

fluorescence microscopy, performed on a VT-Infinity3 confocal module from VisiTech International, mounted on a Nikon Ti-U inverted microscope and equipped with a Hamamatsu ORCA-Flash 4.0 sCMOS camera as the detector. For each sample we capture 2500 three-dimensional xyz-image stacks at 2 Hz and a field-of-view of $205 \times 205 \times 75$ voxels, with voxel dimensions of $0.25 \times 0.25 \times 0.33 \mu\text{m}^3$. In addition, to increase the data range towards higher frequencies we also capture 30,000 two-dimensional slices at a frequency of 20 Hz. The two-dimensional images are used for the calculations of the self-intermediate scattering function. We analyse the resulting image data sets with standard particles locating algorithms to extract the particle centroid positions and time trajectories from the images with sub-pixel resolution, $\sim 30 \text{ nm}$ [9].

In accordance with previous experimental studies of colloidal glasses [10, 11], we empirically identify the glass transition as the volume fraction, ϕ , where the ratio between the timescales of cage-breaking, τ_α , and rattling of particles inside their cages τ_β equals 10^5 — $\tau_\alpha/\tau_\beta = 10^5$. We locate this point at $\phi_g \approx 0.35$.

Results & Discussion

In the previous chapter we calculated the normalised dynamical connectivity function $Z(\tau)/Z_0$ directly from known particle positions from experimental data. The dynamical connectivity $Z(\tau)$ describes how the number of load-bearing particles surrounding a probe particle at time 0 evolves with time as they diffuse and exchange with neighbouring particles; Z_0 is $Z(\tau = 0)$, the static number of load-bearing neighbours. Together they give information about the erosion of particles cages averaged over all particles in the sample. This approach is direct and straightforward but it is limited by the need for particle locations and suffers from deviations due to experimental errors such as particles which are lost during the tracking algorithm. It would therefore be useful to investigate other means of calculating the ensemble averaged number of nearest neighbours of a particle. It is well known that the static number of nearest neighbours, Z_0 , can be defined in terms of $g(r)$, by the following relation:

$$Z_0 = 4\pi\rho \int_0^{R_c} g(r)r^2 dr \quad (5.1)$$

where R_c is a cut-off distance that is often set equal to the first minimum in the amorphous $g(r)$. In the case of close-packed systems $Z_0 \simeq 12$ in three dimensions and $Z_0 \simeq 6$ in two-dimensions. However, our system

Figure 5.1 – Static number of nearest neighbours $Z_0 \equiv Z(\tau = 0)$ as function of volume fraction ϕ . We calculate Z_0 by integration of the first peak in $g(r)$ according to equation 5.1.

is not close-packed. In a Wigner system which is stabilised by long-ranged repulsive interactions, Z_0 represents the number of bonds that are strong enough to have a load-bearing property. With the choice of R_c equal to the first minimum distance in $g(r)$ we find $Z_0 \simeq 15$, well above the Maxwell isostatic condition in three-dimensions of $Z_0 = 6$ (Fig. 5.1). The fact that we find the same value over the entire range of measured volume fractions indicates that static structure alone is not enough to make predictions about the glass transition. While $Z_0 = 15$ is well above the Maxwell isostatic condition, the samples flow as liquids at the lowest ϕ measured. Clearly, Z_0 is not the appropriate parameter with which to evaluate rigidity; Z_0 measures the structural integrity at infinity frequency, $\omega = \infty$. Rather, it is the response at finite frequency that determines the response of a system as either a liquid or a solid. The response at a finite frequency is captured by $Z(\tau)$, it is this metric that we need to measure.

For our prediction it is thus vital to know $Z(\tau)/Z_0$; $Z(\tau)$ is accessible from a generalisation of the radial distribution function: $\rho g(r) = G_d(r, \tau = 0)$ —the radial distribution function $g(r)$ is the instantaneous distinct van Hove function.

The van Hove space-time correlation function [12]:

$$G(r, t) = \frac{1}{N} \left\langle \sum_{i=1}^N \sum_{j=1}^N \delta(\mathbf{r} + \mathbf{r}_j(0) - \mathbf{r}_i(t)) \right\rangle \quad (5.2)$$

gives the probability that, if there is a particle i at the origin at time 0, there will be another particle j at a distance r at time t [13]; the full function does not differentiate between the cases where $i = j$ and $i \neq j$. However, the van Hove correlation function can be split into two contributions, the self-part $G_s(r, t)$ and the distinct part $G_d(r, t)$, respectively. The self-part represents the probability of finding the particle, originally taken to be at the origin, at a distance r at time t . The distinct part predicts the likelihood of finding another particle at a distance r at time t . The self part is the probability that particle j is the same as particle i , whilst the distinct part describes the case where they are two different particles.

At time $t = 0$ the van Hove correlation function reduces to the static particle-particle autocorrelation function:

$$G(r, t = 0) = \delta(\mathbf{r}) + \rho g(r) \quad (5.3)$$

where the Dirac delta function comes from the self-part, while $g(r)$ is the standard radial distribution function arising from $G_d(r, t)$. Hence, $G_d(r, t = 0) = \rho g(r)$. Here ρ is the particle number density.

The definition of the average number of load bearing bonds (Equation 5.1) can be extended to the dynamic case, by replacing the static distribution function $\rho g(r) = G_d(r, t = 0)$ with the time-dependent one,

$$G_d(r, t),$$

$$Z(\tau) = 4\pi \int_0^{R_c} G_d(r, t) r^2 dr \quad (5.4)$$

provided that a nearest-neighbour peak is identifiable in the space-dependent part of $G_d(r, t)$.

$Z(\tau)$ quantifies how an initial configuration of load-bearing bonds connected to a central probe particle erodes with time due to particle rearrangements. While at each point in time Z_0 remains roughly constant, neighbours swap, leading to broken bonds and new ones formed. $Z(\tau)$ measures only the remaining bonds, as this is the mechanism of stress relaxation and thus dictates the rigidity of the sample.

Figure 5.2 – (A) Decay of the normalised coordination number $Z(\tau)/Z_0$ as calculated from the van Hove functions, for different volume fractions (left to right) $\phi = 0.18, 0.22, 0.26, 0.28$, and 0.31 . Solid lines are double stretched exponential fits. (B) van Hove correlation functions $G(r, t)$ for a glassy liquid at $\phi = 0.31$ at $t = 0$ (black circles), 50 (red triangles), 100 (blue squares) s.

To compute $G(r, t)$ from our experimental data we cross-correlate the particle locations in snapshots of the structure rather than working with the data in which particle trajectories have been linked (Fig. 5.2b). We do so to ensure proper statistics and to avoid errors introduced in the determination of $Z(\tau)/Z_0$ since the particle linking algorithm will inevitably lose some particles if their position cannot be determined in every subsequent frame of the confocal microscopy data. While we take care in our experiments to avoid these artefacts as much as possible, they can never be completely suppressed in three-dimensional imaging. The artificial loss of particles would lead to the under-counting of particle neighbours and thus introduce error in the van Hove function. Rather, using unlinked location data gives a much higher accuracy in the determination of $Z(\tau)$ from experimental data. However, as a consequence, self-contributions also appear in the van Hove as a peak which grows with t centred at $r = 0$ (Fig. 5.2B). To correct for these self-contributions to $G(r, t)$ we introduce $-G(r_0, t)$ in the integral (equation 5.4) as a first-

Figure 5.3 – Computer-generated bond network reconstructions of our experimental data showing the connectivity erosion at different lag times for $\phi = 0.31$ at $t = 0$ s (**A**), $t \sim \tau_B = 10$ s (**B**) and $t = 250$ s (**C**). Intact bonds are rendered in blue, while broken bonds are highlighted in green. The small spheres represent the particles and are colour coded either green or purple depending on whether their number of load-bearing neighbours is lower or higher than 6 respectively.

order correction. The corrected integral thus becomes:

$$Z(\tau) = 4\pi \int_0^{R_c} [G(r, \tau) - G(r_0, \tau)] r^2 dr \quad (5.5)$$

To illustrate the concept of dynamical bond erosion we reconstruct computer-generated renderings of our experimental system to show the percolated network of load-bearing bonds. We colour code broken bonds in green and plot the network structure as a function of lag time. At a lag time $\tau = 0$, this shows the static connectivity structure of the suspension, as shown in Fig. 5.3A. All load-bearing bonds are still intact and most particles have more than 6 of these bonds. As time progresses, cages reshape and bonds break. We see how the initially highly connected structure gradually erodes as time progresses, until an unconnected structure, with a few intact clusters of interconnected particles, remains (Fig. 5.3C). At the Brownian frequency some bonds have rearranged but there is still a percolating network present of load-bearing bonds (Fig. 5.3B). This sample would thus classify as solid at a frequency $\omega_B = 0.1$ Hz. At lower frequencies $\omega \ll \omega_B$ erosion leads to $Z(\tau) < 6$ and thus a liquid response. Rigidity in such systems is thus a frequency dependent concept.

We find that the decay in $Z(\tau)/Z_0$ slows down rapidly as the particle volume fraction is increased (Fig. 5.2A), indicating a ϕ -controlled slowing down of the structural dynamics. These data can be described by a stretched exponential decay with a stretch parameter γ : $Z(\tau)/Z_0 \sim \exp(-t/\tau_Z)^\gamma$ (Fig. 5.2A, solid lines). The value of γ is close to unity at low volume fractions, as expected for the simple diffusion of particles in a viscous medium, but decreases well below unity as the density in the system is increased and approaches the glass transition, which we identify

to occur around $\phi \approx 0.35$ (see Materials & Methods and chapter 4 for details). In these viscoelastic suspensions, where caging effects become pronounced, the particle motion is known to become strongly inhomogeneous in both space and time [14]. This leads to a distribution of sub-populations at any given correlation time, each of which may exhibit a Gaussian displacement probability resulting in simple exponential decays, but whose ensemble-average exhibits a broad distribution, resulting in a stretched-exponential decay. Thus, γ is taken as a measure for the extent to which the particle motion is inhomogeneous in space and time [11].

Unfortunately, calculating $G(r, t)$ still relies on knowledge about precise particle locations. However, the Fourier transform of the van Hove correlation function gives the intermediate scattering function which is an experimentally accessible quantity even when individual particles, atoms, or molecules cannot be tracked, e.g. by means of light or neutron scattering:

$$F(\mathbf{q}, t) = \int d^3\mathbf{r} G(r, t) \exp(-i\mathbf{q} \cdot \mathbf{r}) \quad (5.6)$$

The intermediate scattering function can also be split into a self and a distinct part, $F(\mathbf{q}, t) = F_s(\mathbf{q}, t) + F_d(\mathbf{q}, t)$ which are the space-Fourier transform of $G_s(r, t)$ and of $G_d(r, t)$, respectively [15].

To evaluate cage dynamics from these Fourier space metrics, it is necessary to resort to theories of many-particle dynamics in dense liquids and glasses. Mode-coupling theory provides such a theory for the intermediate scattering function $F(\mathbf{q}, t)$. In practice, MCT derives an equation of motion for $F(\mathbf{q}, t)$ which is formally analogous to a generalised Langevin equation with a memory-kernel which provides a feedback mechanism to slow down the correlated particle motion [16]. The approach based on MCT predicts that the time-decay of the intermediate scattering function for long times is dominated by the self-part and features a stretched-exponential decay [16, 12]:

$$F(\mathbf{q}, t) \sim \exp(-t/\tau_c)^\beta \quad (5.7)$$

where τ_c is the α -relaxation time which is associated with substantial restructuring of the glassy cage. Using the Vineyard approximation [17] (see Appendix for details):

$$F(\mathbf{q}, t) \simeq S(\mathbf{q})F_s(\mathbf{q}, t) \quad (5.8)$$

it follows that the distinct part has the same time-dependence as the self-

part and the total $F(\mathbf{q}, t)$:

$$F_d(\mathbf{q}, t) \simeq [S(\mathbf{q}) - 1]F_s(\mathbf{q}, t) \simeq \frac{[S(\mathbf{q}) - 1]}{S(\mathbf{q})}F(\mathbf{q}, t). \quad (5.9)$$

Here $S(\mathbf{q})$ is the static structure factor, i.e. the space Fourier transform of $g(r)$ (See Appendix for static structure factors from our experimental data). Hence, assuming that $F(\mathbf{q}, t) \sim \exp(-t/\tau_c)^\beta$, we then have

$$G_d(r, t) \simeq \frac{[S(\mathbf{q}) - 1]}{S(\mathbf{q})} \int d^3\mathbf{q} F(\mathbf{q}, t) \exp(+i\mathbf{q} \cdot \mathbf{r}). \quad (5.10)$$

Since the inverse Fourier transform over space leaves the time-dependence unaltered, the time-dependence of $G_d(r, t)$ follows as:

$$G_d(r, t) \sim \exp(-t/\tau_c)^\beta \quad (5.11)$$

and therefore also the integration over the first peak of $G_d(r, t)$ leaves the following dependence for the dynamic mean nearest-neighbour number:

$$Z(\tau) \sim \exp(-t/\tau_Z)^\gamma. \quad (5.12)$$

Thus, if the Vineyard approximation is valid, $\gamma \equiv \beta$, the time-scaling of the self-intermediate scattering function $F_s(\mathbf{q}, t)$ and $Z(\tau)$ must be identical. If the time-dependence is indeed identical the Vineyard approximation offers a means to probe the connectivity transition, which we propose to be at the heart of vitrification in strongly correlated systems, from scattering experiments. While the Vineyard approximation has been tested for simple liquids [18, 4] and was found to decay too rapidly at short time-scales, it has never been tested close to or beyond the glass transition.

The central test for the Vineyard approximation in this system thus becomes whether the exponents (β and γ) and the characteristic decay times (τ_c and τ_Z) match for the long-time exponential description of $F_s(\mathbf{q}, t)$ and $Z(\tau)$ (equations 5.7 & 5.12).

We calculate $F_s(\mathbf{q}, t)$ directly from experimental particle tracks as:

$$F_s(\mathbf{q}, t) = \langle \exp(i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]) \rangle \quad (5.13)$$

which we calculate at $|\mathbf{q}|$ equal to $\frac{2\pi}{r_1}$, where r_1 is the position of the first peak in $g(r)$, to probe self-diffusion of the particles only. We average over 16 different radial orientations of the wave-vector $\mathbf{q}$ and over all the particles in the system. The resulting self-intermediate scattering function $F_s(\mathbf{q}, t)$ shows two decays, as expected for dense suspensions approaching their solid-liquid transition (Fig. 5.4A). A decay at short lag times evidences the β -relaxation, which results from the vibration of particles inside the cage formed by its neighbours.

A second decay at longer lag times is the hallmark of α -relaxations which are typically understood as cage-breaking events that provide the particle with a means to perform translational motion over larger length scales. The two decays are characterised by their decay times, τ_β and τ_α respectively. We extract the decay times by fitting the experimental $F_s(\mathbf{q}, t)$ to a double stretched exponential[10], of the form $F_s(q, t) = A \exp[-(t/\tau_\beta)^\delta] + (1-A) \exp[-(t/\tau_\alpha)^\beta]$. The second stretched exponential corresponds to the long-time behaviour of $F(\mathbf{q}, t)$ described in equation 5.7. The long-time dependence of $F(\mathbf{q}, t)$ is dominated by $F_s(\mathbf{q}, t)$. Therefore equation 5.7 can be written as: $F_s(\mathbf{q}, t) \sim \exp(-t/\tau_\alpha)^\beta$. As the volume fraction, ϕ , increases, τ_α increases over several decades in time (Fig. 5.4A inset).

Figure 5.4 – (A) Intermediate scattering functions $F_s(q, t)$ at $q = 2\pi/r_1$ for (top to bottom) $\phi = 0.49, 0.35, 0.28, 0.31, 0.26, 0.22$, and 0.18 . Solid lines are fits to a double stretched exponential decay as explained in the main text. **(inset)** Characteristic relaxation times for α -relaxation from $F_s(q, t)$ (circles), and $Z(\tau)/Z_0$ relaxation (triangles). Solid line is VFT fit of the form $\tau_\alpha = \tau_0 \exp \frac{A\phi}{\phi_0 - \phi}$, with $\tau_0 = 3.5$, $A = 1.7$, and $\phi_0 = 0.4$. Error bars are the standard errors of the fitting procedure. **(B)** Stretch exponents from the stretched-exponential fits to $F_s(k, t)$ (β , triangles) and $Z(\tau)/Z_0$ (γ , circles).

We now have all the information we need to test the applicability of the Vineyard approximation to gain information needed for $Z(\tau)/Z_0$ from easily accessible scattering experiments. For the approximation to be useful the characteristic decay times and the stretch-exponents of the self-intermediate scattering function and the dynamical coordination number should be similar and follow the same relation with ϕ . We plot the stretch-exponents, β and γ for $F_s(\mathbf{q}, t)$ and $Z(\tau)/Z_0$ and find that the two exponents are the same within experimental errors and decay in unison (Fig. 5.4B). We find that the characteristic decay times of both quantities also follow the same quantitative dependence on volume fraction ϕ (Fig. 5.4A inset).

The equality in the two quantities holds until ϕ is close to the glass transition at $\phi \approx 0.35$. At the point of full dynamical arrest and higher, the Vineyard approximation clearly breaks down; the approximation is

based on the assumption that the displacement probability of a particle i in relation to all other particles can be captured by the average self-displacement probability of a single particle, in the shape of the self part of the van Hove function, $G_s(r, t)$. This approach assumes that the displacement of a particle i is uncorrelated to the movement of other particles. In a highly dense system close to the glass transition this assumption clearly breaks down.

Furthermore, the Vineyard approximation is known to predict a too rapid decay at short times[18]. However, since we are only interested in the long time decay characteristics we feel that in the case of highly charged colloidal liquids the Vineyard approximation gives a reasonable way to determine the necessary parameters for our prediction from experimentally accessible scattering experiments.

Conclusions

In this chapter we have opened up our predictions from the previous chapter to systems from which we can not directly get access to the location of every particle in the system. We have extended our method to calculate the dynamical coordination number from a straightforward method based on experimental particle data to a method accessible with scattering methods.

We rely on the Vineyard approximation to calculate the distinct-intermediate scattering function, $F_d(\mathbf{q}, t)$, from the self-part and the static structure factor. The distinct-intermediate scattering function is related to the distinct van Hove function via an inverse-Fourier transform. It is the distinct van Hove function that holds information about the mean dynamical coordination number of the system under study.

While this approach is potentially highly useful, it relies on the Vineyard approximation. This method relates the distinct part to the self part of the intermediate scattering function and is known to predict a decay which is too fast at short times due to the obvious errors inherent to the approximation of choice. However, in our case we are only interested in the decay characteristic on long time-scales. To confirm the validity of the approximation we compared the characteristic relaxation times and stretch exponents of both the dynamical coordination number and the self-intermediate scattering function. We found a match between these two quantities within experimental error. This suggests that for our purposes the Vineyard approximation is an acceptable path. The validity of the Vineyard approximation in our system will allow us to expand our predictions and test them in systems which are otherwise inaccessible, such

as atomic or molecular systems. This new method will allow for the use of scattering methods to gain information about dynamical connectivity.

The classic Vineyard approximation used in this chapter is only the simplest form. Several improvements have been made to introduce a more realistic function instead of $G_s(r, t)$ to capture the movement of particles. These improvements include the introduction of a delay in the convolution of $g(r)$ with $G_s(r, t)$ [18] and replacing $G_s(r, t)$ with $G_{sd}(r, t)$ [19] which takes into account correlations between pairs of particles. Both extensions can significantly improve short-time predictive capabilities.

The Wigner colloidal system we study here is akin to strongly correlated systems of electrons or ionised atoms, in that interactions range beyond the first coordination shell. This raises the question how the effects we observe depend on the interactions between the building block of the glass. With the method developed in this chapter we can now start to answer some of these questions.

Appendix

Vineyard approximation

The full van Hove function can be written as a sum of self and distinct parts: $G(r, t) = G_s(r, t) + G_d(r, t)$. The self part, which takes into account only the displacements of identical particles, is easier to calculate; this is in contrast with the distinct part. The Vineyard approximation is an attempt to express the distinct part of the van Hove function as a convolution of the static structure of the system with a function which described the probability of movement of a particle from position $\mathbf{r}$ to $\mathbf{r}'$ during a time t , $H_0(\mathbf{r} - \mathbf{r}', t)$. This gives the relation:

$$G(\mathbf{r}, t) = G_s(\mathbf{r}, t) + \int g(\mathbf{r}') H_0(\mathbf{r} - \mathbf{r}', t) d\mathbf{r}' \quad (5.14)$$

The approximation is made by making the ansatz that $H_0(\mathbf{r} - \mathbf{r}', t)$ can be approximated by the self-part of the van Hove function, which describes the probability of a particle to move from $\mathbf{r}$ to $\mathbf{r}'$ without knowledge of the position of other particles: $H_0(\mathbf{r} - \mathbf{r}', t) \simeq G_s(\mathbf{r} - \mathbf{r}', t)$ [17]:

$$G(\mathbf{r}, t) \simeq G_s(\mathbf{r}, t) + \int g(\mathbf{r}') G_s(\mathbf{r} - \mathbf{r}', t) d\mathbf{r}'$$

$$G_d(r, t) \simeq \int g(\mathbf{r}') G_s(\mathbf{r} - \mathbf{r}', t) d\mathbf{r}'$$

under a Fourier transform this becomes:

$$F_d(\mathbf{q}, t) \simeq S(\mathbf{q}) F_s(\mathbf{q}, t) \quad (5.15)$$

We are interested in the time dependence of the intermediate scattering function; given equation 5.15 and since $F(\mathbf{q}, t) = F_s(\mathbf{q}, t) + F_d(\mathbf{q}, t)$, F_s and F_d clearly must have the same dependence on t .

Then adding F_s to the left-hand-side of equation 5.15, clearly cannot change the time-dependence. Therefore we can also write the Vineyard approximation as $F(\mathbf{q}, t) \simeq S(\mathbf{q}) F_s(\mathbf{q}, t)$, which will have the same dependence on t ; within some prefactor which is independent of t .

Static structure factor

Figure A5.1 – Structure factors for Wigner glasses. (A–C) Calculated, from experimental particle locations, two-dimensional structure factors, $S(q_x, q_y)$, for, left-to-right, $\phi = 0.49$, 0.28, and, 0.22. (D–F) Radially averaged structure factors as in (A–C).

We can calculate the static structure factor $S(\mathbf{q})$, as:

$$S(\mathbf{q}) = \frac{1}{N} \left| \sum_{j=1}^N \mathbf{e}^{-i\mathbf{q}\mathbf{R}_j} \right|^2 \quad (5.16)$$

We perform the calculations on our experimental data and plot its two-dimensional projection, $S(q_x, q_y)$, and radial average in Fig.A5.1. The structure factors clearly shows a liquid-like order, evident from the characteristic Debye–Scherrer rings and absence of periodic Bragg peaks in the radial average (Fig. A5.1). These results corroborate our findings in the previous chapter, where we also found no signs of structural order in the real-space radial distribution function, $g(r)$.

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DECOUPLING OF THE BINARY GLASS TRANSITION OBSERVED WITH CONTRAST VARIATION MULTISPECKLE DIFFUSING- WAVE SPECTROSCOPY

6

In the study of colloidal glasses, crystallisation is often suppressed by leveraging size polydispersity, ranging from systems where particle sizes exhibit a continuous distribution to systems composed of particles of two distinct sizes. The effects of the disparities in size of the particles on the colloidal glass transition are not yet completely understood. Especially the question of the existence of a decoupled glass transition between the large and small population remains. In order to measure colloidal dynamics on very long time-scales and to disentangle the dynamics of the two populations we employ contrast variation multispeckle diffusing wave spectroscopy (MS-DWS). With this method we aim to analyse the effect of size ratio, $a = r_{\text{small}}/r_{\text{large}}$, on particle dynamics near the glass transition of a binary colloidal system. We find that both for long (α –) and short time (β –) relaxation the dynamics of the small particles either completely decouple from the large ones ($a = 0.2$), moving freely through a glassy matrix, or are identical to the dynamics of the larger sized population ($a = 0.37$ & 1.44). For a size ratio of 0.37 , we find a single glass transition for both particle populations. The postulated double glass transition is not observed.

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Introduction

GLASSY solids remain an intriguing state of matter as even after decades of study many questions are left open; as is evident from our description and analysis of the behaviour of a highly charged colloidal glass in chapter 4 of this thesis. In general terms, whenever a liquid transitions into a solid state it is often characterised by a distinct change in both the dynamical behaviour of the system and in its structural features. For example, whereas a liquid state has an isotropic structure, the transition into a crystalline solid state gives rise to a highly anisotropic structure with well-defined ordered positions for the constituent parts of the system, be they colloidal particles, molecules or atoms. In the glass transition, a special case of a liquid-to-solid transition, there is no appearance of anisotropic and ordered structure. Instead, the system retains its isotropic and disordered structure, characteristic of the liquid phase, throughout the transition while its dynamics slow down strongly. The lack of clear structural signs for the liquid-glass transition make it elusive to understand.

The dynamical slowdown that signals the glass transition often takes the form of a super-exponential increase of the sample's relaxation time with an increase in volume fraction [1, 2, 3, 4]; behaviour captured by the phenomenological Vogel-Fulcher-Tammann (VFT) equation [5, 6]: $\tau = \tau_0 \cdot \exp \frac{A\phi}{\phi_0 - \phi}$. More fundamental and accurate predictions have been made by mode-coupling theory (MCT), which has proved successful at predicting dynamics as systems approach their glass transition. However, experimental deviations have been found close to the transition point [7, 8]. The experimental study of colloidal glasses is challenging since a system composed of colloidal particles of identical size tends to crystallise easily within experimental time-scales, bypassing the meta-stable glass phase of interest. The quench-rates needed to vitrify mono-disperse non-hard sphere glasses have not been achieved in experiments [9]. A common strategy to prevent a sample from crystallising is to employ size polydispersity [10]. Particles with an ensemble size polydispersity $> 6\%$ are effectively prevented from crystallising [11, 10]. However, the resulting large distribution of particle radii makes analysis often more difficult. Therefore, experiments often use two distinct sizes instead of a continuous distribution [12]; with a size ratio of, $a = \frac{r_S}{r_L}$ with r_S and r_L being the radius of the small and large particle population

Figure 6.1 – Depending on the size ratio between the probe particles and the matrix we expect different dynamical behaviour: Probes of sizes comparable to the matrix particles will follow the behaviour of the matrix and feel a glass transition on concomitant time-scales. Particles much smaller than the matrix particles will be able to move around even after the matrix has undergone dynamical arrest.

Figure 6.2 – (top) At short time-scales particles vibrate inside the cage formed by their surrounding particles (coloured grey); cage-rattling or β -relaxation. (bottom) If we wait much longer particles can escape their cages; cage-breaking or α -relaxation.

respectively. The ability of such a binary system to suppress crystallisation depends on the size and mixing ratio. A particularly effective glass former is found at a 1:1 ratio of particles with $a = 0.17$ [13].

The use of two or more differently sized components to form a glassy state is also well known in bulk metallic glasses (BMG); while binary BMGs are known, often a more complex geometrical alloy is used to ensure ultimate stability of the glass phase. The development of metallic glasses relies on stabilising the super-cooled liquid state up to such an extent that the glass transition can be made with an achievable cooling rate; as low as 0.10 K/s for $\text{Pd}_{40}\text{Cu}_{30}\text{Ni}_{10}\text{P}_{20}$ [14, 15].

Simulations and mode-coupling theory predictions (MCT) [16, 17, 18, 19] on the effects of binary mixtures on dynamical arrest show a decoupling in the dynamical behaviour of large and small particles, giving rise to two distinct transitions; the larger species arrest at lower volume fraction indicated by the appearance of a finite localisation length, while the smaller species retain a finite, though reduced, mobility. Evidence for this decoupling have also been observed in recent experiments using confocal microscopy on a polydisperse colloidal hard-sphere system [20]. So far the effect of the size ratio between large and small particles on the predicted decoupling remains experimentally unexplored.

One of the large challenges to experimentally investigate glassy phenomena is the inherently large range of time-scales present in the dynamics of very dense systems. In dense suspensions, particles are effectively caged by their neighbours. It is the fast diffusive movement of particles within this cage, β -relaxation or ‘cage-rattling’, that form the fast dynamics. On much longer time-scales particles will escape this cage by means of α -relaxation or ‘cage-breaking’, and diffuse through the system (Fig. 6.2). It is these two modes of motion that give rise to the large range of time-scales involved in the problem, often spanning many decades. This is only exacerbated by a possible decoupling between the dynamical behaviour of the large and small population. The usual experimental techniques used to investigate colloidal glasses are either microscopy, especially confocal microscopy, or light-scattering techniques such as dynamic light scattering (DLS). Confocal microscopy offers the possibility to visualise and follow individual particles and thus also give a means to discriminate between the two particle populations. However, microscopy is limited to a relatively small window of time-scales which can be investigated; both fast timescales ($< 10^{-3}$ s) and very long time-scales ($> 10^4$ s) are difficult to access, due to the limited capture rate of cameras and the limit on storage space available for images. Light-scattering techniques are better suited to access the wide range of time-scales. However, information about the distinct particle populations is lost and samples have to be optically transparent; which is often a challenge for a densely packed sample.

In order to tackle both issues, time-scales and of the necessary optical properties of the sample, we employ Diffusing Wave Spectroscopy (DWS) [21, 22]. This technique has been developed specifically to measure dynamical properties of samples which are so turbid that light will scatter many times in the sample before reaching the detector. In fact, the analysis is based on the assumption that photons scatter so many times that their path through the sample can be described as a diffusive walk. We specifically use a dual-detector variant of the DWS technique to extend our time window across seven decades [23]. A photon-multiplier tube (PMT) and charge-coupled device (CCD) chip both detect the scattered light. The PMT detector is used to detect correlations in the scattered light on very short time-scales ($10^{-4} \text{ s} \leq \tau \leq 10^1 \text{ s}$) while the CCD chip, which provides as many detectors as there are pixels on the chip, can correlate scattered light on much longer time-scales ($\tau > 10^1 \text{ s}$). If the necessary precautions are taken with respect to vibrations in the setup and the stability of temperature and laser intensity the PMT detector could also be used for times higher than 10^1 s . However, the non-ergodic nature of the glass requires us to average in space as well as in time. With a CCD detector this is easy since we capture multiple speckles in the two dimensional detector plane; for a PMT this requires the use of a secondary cell with slowly diffusing scatterers. This effectively limits the times accessible to the PMT detector to the characteristic decay time of the secondary cell. We describe the secondary cell in more detail below.

Our search for a decoupled glass transition in a binary system depends on our ability to measure the dynamics of the two populations separately. To do so, we use the method of contrast variation, where we selectively match the contrast of two species in the system. We use poly(N-isopropylacrylamide) (PNIPAM) microgel particles for one species and polystyrene particles for the other. PNIPAM microgel particles have an index of refraction very close to that of the aqueous medium, $n_w = 1.33$, as they are composed mainly of water ($\sim 95\%$) [24], while polystyrene differs a lot, $n_{PS} = 1.59$ [25]. Therefore, DWS will detect a weighted averaged signal heavily biased towards light scattered by the polystyrene population; the contribution from the microgels is negligible.

By varying the size of the polystyrene particles in the microgel matrix we investigate the dynamics, over seven decades in time, during the glass transition of binary mixtures at several size ratios, $a = \frac{r_{PS}}{r_{PNIPAM}}$. We find that the dynamics of binary mixtures is itself binary in nature: for a small size ratio, $a = 0.2$, the dynamics of the small particles are completely decoupled on all time-scales from the larger microgel matrix; showing only hindered diffusion at long times-scales. Intermediate to large size ratios, $a = 0.37$ & $a = 1.44$ show identical dynamics to the microgel mat-

rix. We observe no double glass transition where separate particle populations experience the glass transition at different packing fractions, even though this was predicted to occur for $a = 0.35$ [16, 17, 18, 19].

Materials & Methods

Particle synthesis

All chemicals are bought from Sigma-Aldrich and are used as received.

We synthesise poly(N-isopropylacrylamide) (PNIPAM) particles with diameter, $r = 0.45 \mu\text{m}$ via an aqueous surfactant-free radical precipitation copolymerization according to methods as described in [26]. We clean the particles using subsequent centrifugation, washing and resuspension steps. After completing the cycle 3 times we finally suspend the particles in 1 mM NaOH; this charges the acrylid acid functional groups in the microgels and swells the particle. In the case of PNIPAM particles this swelling is known to be temperature dependent as the PNIPAM polymer has a lower critical solution temperature around 37°C [27]. Indeed we observe shrinking of the particles as the temperature changes from $15\text{--}45^\circ\text{C}$. However, instead of a sharp transition at 37°C we find a gradual decrease over the entire temperature range (Fig. 6.3). To get a sample of very high packing fraction, which we can dilute in further experiments, we centrifuge the microgels at 25,000 g for five hours. The volume fractions of a heavily diluted sample can be determined using an Ubbelohde capillary viscometer thermostatted at 20°C and referenced to the viscous properties of toluene. Via the Einstein relation, $\eta_r \equiv \frac{\eta_{\text{sample}}}{\eta_{\text{toluene}}} = 1 + 2.5\phi$, we arrive at a volume fraction. We extrapolate the volume fraction from the dilute limit to higher concentrations. Since the particle size may change due to osmotic deswelling, this leads to an apparent packing fraction ζ . With this technique we find packing fractions of $\zeta = 1.12$ and $\zeta = 1.4$ for two prepared stock samples, from which dilutions are made.

As probe particles we use polystyrene (PS) particles with radii, $r = 0.09 \mu\text{m}$, $r = 0.17 \mu\text{m}$ & $r = 0.65 \mu\text{m}$, prepared using emulsion polymerisation according to the method described in reference [28], with the exception of the largest probe particles, which we synthesised using dispersion polymerisation according to reference [29]. We clean the polystyrene probe particles by repeated centrifugation and resuspension steps in a 1 mM NaOH solution. The three different combinations of microgel matrix and one size of probe particles are diluted to a final polystyrene volume fraction $\phi_{PS} = 0.01$ with a high microgel packing fraction

Figure 6.3 – Temperature dependence of PNIPAM microgel particles. Particle radius, r (nm), is measured using dynamic light scattering of a highly diluted sample. We scan the temperature range 15–45 °C up and down and find perfect agreement of both directions. The microgel particles appear to gradually shrink by a factor of 2.5 over the entire temperature range.

$\zeta_{\mu\text{gel}} > 1.0$.

Here we should make a distinction between the volume fraction, ϕ , and the packing fraction, ζ ; both are the ratio between the volume of the dispersed phase and the volume of the total sample. Since our polystyrene probe particles are solid particles which can not overlap or compress it is appropriate to use volume fraction, ϕ , which is only defined on the interval $[0, 1]$. This is in contrast to the microgel matrix; where particles are able to deswell causing the apparent packing fraction to be higher than unity, in this last case we prefer to speak in terms of a packing fraction, ζ .

Constrast Variation Multi Speckle Diffusing Wave Spectroscopy

Diffusing wave spectroscopy background

It is often challenging to disentangle the dynamics of individual species in systems in which multiple components interact over an extended time window and with enough signal to gain reliable data. For example, conventional dynamical light scattering (DLS) breaks down when samples get too dense as photons no longer undergo just one scattering event due to the density of scatterers present. One way to overcome this issue would be to match the index of refraction of the entire system to that of the containing vessel, thereby reducing the amount of scattering events. While this method has been successful and has produced insights in dense systems [7], a different light scattering method exists which inverts the notion of single scattering and makes the assumption that light travelling through the sample undergoes many scatter events before exiting; Diffusing Wave Spectroscopy (DWS). Furthermore, with DLS we are lim-

Figure 6.4 – Even though the incoming beam is at a constant position; due to many small differences in particle positions over time the scattering path will significantly change and the interference will produce speckle patterns which vary in time depending on the movement of the scatterers.

ited to a small range in optical densities that we can measure, severely hampering our ability to use contrast variation efficiently. DWS allows for measurements in a much broader optical density range, giving much more room for contrast variation techniques.

In DWS there are two governing assumptions about the nature of light propagation in a sample. Firstly we take it that photons undergo so many scatter events on their path through the sample that any correlation in their directionality is lost so that we can describe their motion in term of random walks. Secondly, since each photon undergoes many scattering events and the paths become randomised such that we lose the angle dependence on the scattering intensity which exists in DLS (Fig. 6.4). We measure the temporal autocorrelation function of the scattered light and interpret this to get information about the dynamics of the scatterers.

There are two major length scales involved in DWS; l and l^* , the photon mean-free path and the photon transport mean-free path, respectively. The photon mean-free path, l , represents the average distance between two scattering events, while l^* is equal to the distance a photon must travel before all correlation in its travelling direction is lost, consisting of a path several times l . For a system with a homogeneous distribution of scatterers we can describe the photon mean-free path as $l = (\rho\sigma)^{-1}$ with ρ the number density of scatterers and σ the scattering cross-section of a single scatterer; this relates to l^* via:

$$l^* = \frac{l}{\langle 1 - \cos \theta \rangle} \quad (6.1)$$

where θ is the scattering angle of a single event and the brackets, $\langle \dots \rangle$, average over all scattering events. l^* is a sample specific parameter which we need to know for every sample under study to be able to analyse the data obtained. If we say that the light has to travel a distance equal to the path length of our cuvet, L , before being detected there would have been approximately $(L/l^*)^2 (l^*/l)$ scattering events. If $L \gg l^*$ we ensure that we measure in the multiple scattering limit and the DWS approach is valid. In practical terms this means $L \geq 10 \cdot l^*$, with l^* typically on the order of $50 - 500 \mu\text{m}$.

Figure 6.5 – A typical speckle pattern as captured by a CCD camera.

The many possible scattering paths cause a distribution in the phases of the photons that are detected. This causes them to interfere constructively and destructively. The resulting complex field manifests itself as a seemingly random pattern of bright blobs (or ‘speckles’) when captured on a CCD chip (Fig. 6.5). Our setup utilises a dual detection setup; with the PMT detector we look at the temporal correlation of a single speckle, while the CCD chip captures multiple speckles — Multi-Speckle DWS. The combination of two detectors allows us to measure the dynamics of

our system over many orders of magnitude in time, thus joining the advantages of these two detection modes.

Both the PMT and CCD based detectors measure light intensity over time, $I(t)$; from this we calculate $g_2(t)$, the intensity autocorrelation function, using a hardware correlator. DWS theory is based on the field autocorrelation function $g_1(t)$, which we can obtain from $g_2(t)$ via the Siegert relation, $g_1(t) = \beta \sqrt{g_2(t) - 1}$. The exact data analysis methods used are described later in this section. Clearly, the resulting field autocorrelation function, $g_1(t)$, depends strongly on the system dynamics — our quantity of interest — and the probability distribution of possible photon paths in the sample. In a general sense this is captured by the central equation in DWS theory for transmission geometry measurements:

$$g_1(t) = \int_0^\infty P(s) \cdot \exp \left[- (2t/\tau) \frac{s}{l^*} \right] ds \quad (6.2)$$

$$t/\tau = 6^{-1} \cdot (k_0^2 \langle \Delta r^2(t) \rangle) \quad (6.3)$$

This equation expresses the field autocorrelation function $g_1(t)$ in terms of the probe particle mean-squared displacement, $\langle \Delta r^2(t) \rangle$, by integrating over the contribution of every possible photon path length, s , to the decay of $g_1(t)$; here $k_0 = 2\pi/\lambda$. Expressions for $P(s)$ can be derived on the basis of diffusion equations and the measuring geometry [30]. For the case of non-interacting and purely diffusing particles in a transmission geometry, $P(s)$ is known and equation 6.3 becomes:

$$g_1(t) = \frac{\left(\frac{L}{l^*} + \frac{4}{3} \right) \sqrt{\frac{6t}{\tau}}}{\left(1 + \frac{8t}{3\tau} \right) \sinh \frac{L}{l^*} \sqrt{\frac{6t}{\tau}} + \frac{4}{3} \sqrt{\frac{6t}{\tau}} \cosh \frac{L}{l^*} \sqrt{\frac{6t}{\tau}}} \quad (6.4)$$

Experimental setup

As the dynamics of glasses involves both fast β -relaxation (cage rattling) and slow α -relaxation (cage breaking) a measurement setup is needed that can probe a wide range of time-scales. We achieve this with a multi-speckle diffusing wave spectroscopy (MSDWS), equipped with two detection pathways. This setup allows us to probe short time-scales with a photo-multiplier tube (PMT) detector and long timescales using a charged coupled device (CCD) camera [23].

Our MS-DWS setup uses a Cobolt Samba diode-pumped solid-state continuous wave (CW) laser, with a maximum output power of 1.5 W. The combination of a rotatable $\lambda/2$ -plate and polarising beam splitter cube (P-BS) gives us fine control of the laser power used for the measurements — the $\lambda/2$ -plate controls the direction of linear polarisation of the

Figure 6.6 – Schematic overview of our MSDWS setup with dual detection. We use an 1.5 W diode-pumped continuous wave solid-state laser with an emission wavelength, $\lambda = 532$ nm. $\lambda/2$ Half-lambda wave plate. **P-B-S** Polarising beam-splitter cube. **BD** Beam dump. **M1 & 2** Broadband mirrors. **10x BE** A ten times beam expander; which in our case is made up out of a single unit from Thorlabs, BE10-532. **D1 & 2** Adjustable diaphragms. **S1** Primary sample holder. **O** $2 \times$ Infinity-corrected objective. **NP-B-S** 50:50 Non-polarising beam splitter cube. **S2** Secondary sample holder for an ergodic correction sample. A functional description of the setup can be found in the main text. **P1 & P2** Polarisation filters.

incoming laser light; the P-B-S cube splits the incoming beam according to the magnitude of its orthogonal polarisation components. The measurement beam is expanded ten times in diameter, to a diameter of 15 mm, using a beam-expander (Thorlabs BE10-532) before we clean up its edges using a diaphragm. The expanded beam is then projected onto the sample which is placed in a cuvette with an optical path length $L = 5$ mm. We measure the transmitted scattered light after collimation with a long working distance $2 \times$ Mitutoyo objective. A non-polarising beam splitter cube splits the scattered light intensity 50:50 with one side leading to our PMT detector and the other one towards a Fastec HiSpec 1 CCD camera — 1280×1024 pixels. In front of both detectors is a polarisation filter, this filter eliminates unscattered or few-times scattered light. The PMT detector has an internal pinhole ensuring we only measure the signal from one speckle. The digital count rate signal from the PMT detector is correlated in time using a hardware correlator unit, ALV-7004/USB. Both the camera and correlator unit are connected to a computer controlling the setup and saving data from both the correlator and camera. A schematic overview of the setup can be found in Figure 6.6.

Two-cell DWS

As we are measuring highly dense vitrified samples which are non-ergodic, we need a second sample cell in front of the PMT detector [31]. In the case of a non-ergodic sample, taking an average over time is no longer equal to taking the ensemble average. Our PMT detector averages over time and thus does not gain a proper ensemble averaged correlation curve, but one that is specific for the location of the speckle; a second sample with an ergodic sample after the primary sample can solve this problem. This sample cell, with an optical path length $L = 2$ mm, contains a suspension of polystyrene particles, radius $r = 0.5 \mu\text{m}$, in glycerol at a volume fraction of $\phi = 0.01$. This second cell acts as a ‘scrambler’ of the incoming light, effectively randomly sampling the ensemble of incoming light scattered by the primary sample under investigation which forces its decorrelation and thus ensures proper normalisation of $g_2(t)$. It has a similar effect as translating the primary sample. Of course, this method limits our detection window for PMT detection by the decay time of the secondary sample. We can tune this limit by controlling the decay time of the second sample via the viscosity of its suspending medium, the thickness of the cell or the concentration of scatterers in the cell.

Signal-to-noise

To maximise the CCD camera detection signal-to-noise ratio we would like to image as many speckles as possible, but if the speckle size becomes too small each pixel may perform an unwanted multispeckle average. The speckle size is determined by the diameter of diaphragm **D2** and its distance to the CCD chip, which can be approximated with the following relation [23]:

$$s \approx \frac{d\lambda}{a} \quad (6.5)$$

where s is the speckle size, d is the distance between the diaphragm and the chip which we set to 15 cm, and a is the diaphragm diameter.

To optimise these settings, we use the procedure outlined in [23]. We measure the y-axis intercept of the correlation function $g_2(0)$ for 2500 distinct measurements of a polystyrene in water sample at several settings for the diameter of the diaphragm between 1 and 5.5 mm. We plot the distribution of intercepts and calculate its signal-to-noise ratio as $\langle g_2(0) \rangle / \Delta g_2(0)$ (Fig. 6.7). Based on these measurements we select a diaphragm diameter, $a = 2.5$ mm for all our subsequent measurements; this choice of diameter maximises the signal-to-noise ratio while still having intercepts close to the theoretical value of $g_2(0) = 2$.

Figure 6.7 – (A) Probability distributions of $g_2(0)$ intercepts for different diameters, a in mm, of diaphragm **D2** as indicated by labels in graph. **(B)** Signal to noise ratio calculated as: the average of the intercepts $\langle g_2(0) \rangle$ divided by the spread of the intercepts $\Delta g_2(0)$, as a function of diaphragm diameter.

Data processing

The data from the PMT is correlated in time using a hardware correlator which gives us the intensity correlation function, $g_2(\tau) - 1$ directly, with the caveat that this represents a convolution of the signal as scattered by the primary sample and the forced-decorrelation by the secondary sample. Via the Siegert relation [32]

$$g_1(\tau) = \beta \cdot \sqrt{g_2(\tau) - 1} \quad (6.6)$$

where β is a setup dependent coefficient which normalises $g_1(t)$ such that $\lim_{t \rightarrow 0} g_1(t) = 1$. Using this relation we arrive at the field autocorrelation function, $g_1(t)$, which we need for further analysis.

Light measured by the PMT has passed through two sample cells in order to deal with the non-ergodicity of the primary sample. The actual measured signal $g_1^M(\tau)$ is composed of signals from both the primary and secondary cell. In the case where there is only a slight to no loss in light intensity between the primary and secondary cell and when the optical thickness of the secondary cell is much lower than the primary cell, the following *multiplication rule* [31] holds:

$$g_1^M(t) = (g_1^P(t)) \cdot (g_1^S(t)) \quad (6.7)$$

In our setup there is an obvious but well-defined loss of intensity between the primary and secondary sample due to the presence of the beam splitter cube. We lose 50% of the light, loss factor $f = 0.5$. In this situation the following conditions have to be true in order for the *multiplication rule* to be valid [31]:

$$\frac{L_{P/S}}{l_{P/S}^*} \gg \frac{4}{3} \quad (6.8)$$

$$\frac{\alpha_{P/S} l_{P/S}^*}{\tanh \alpha_{P/S} L_{P/S}} \ll \frac{3}{4} \quad (6.9)$$

with $L_{P/S}$ and $l_{P/S}^*$ the optical path length and photon transport mean free path respectively for the primary and secondary sample cells, and $\alpha_{P/S}$ the ‘attenuation’ coefficient. Both conditions hold in our case; for $L_{P/S} = 2$ mm and $l_{P/S}^* = \mathcal{O}(100)$ μm the first condition clearly holds, the second condition is generally taken to hold in real life DWS experiments [31]. We therefore conclude that the *multiplication rule* also holds for our experiments. We now get the primary correlation curve $g_1^P(\tau)$ by dividing the measured signal by a correlation curve measured of only the secondary cell $g_1^S(\tau)$, which we measure by simply removing the primary cell and keeping everything else as is with the exception of the laser power which we tune to appropriate levels for the secondary cell.

To analyse the CCD chip data (128×128 pixels from the middle of the chip) we treat every pixel as a separate light intensity detector and calculate the multispeckle averaged $g_2(t, t_0) - 1$ according to equation 6.10.

$$g_2(t, t_0) = \frac{\langle I_i(t_0) \cdot I_i(t_0 + t) \rangle_i}{\langle I_i(t_0) \rangle_i \langle I_i(t_0 + t) \rangle_i} \quad (6.10)$$

where $I_i(t_0)$ is the light intensity measured at the start of the measurement on pixel i , and $I_i(t_0 + t)$ is the light intensity measured t s after the start of the measurement on pixel i . $\langle \dots \rangle_i$ indicates averages over all pixels i in the captured image. This multispeckle averaging allows us to measure without a second ergodic sample in the CCD chip light-path; instead of averaging by scrambling the signal using a second cell we multispeckle average in space directly from the CCD chip to provide the required ergodicity. Similarly to the PMT data we convert the measured intensity autocorrelation function, $g_2(t)$, to the field autocorrelation function, $g_1(t)$, with the Siegert relationship.

Our setup utilises a double detector setup with the aim of increasing our measurement time window. To this end we need to combine the data from the PMT and CCD detector. We start by truncating the data from the PMT at the point where our ergodic second sample starts to decorrelate. This process has a characteristic decay time of $1 \cdot 10^3$ s (Fig. 6.10), we truncate the data at 30 ms which is far from the decorrelation time of the secondary cell but still offers overlap with the CCD camera. The camera operates at a frequency of 500 Hz; our minimal correlation time becomes 2 ms. Combining both data sets gives us an overlap region of more than a

decade between 2–30 ms. To overlap the CCD data with the PMT data we scale the β in the Siegert relation for the CCD data in such a way that we minimise the differences between the two data sets in the overlap region. For all samples this gives us excellent agreement in the overlap region.

Data analysis

The quantity of interest we would like to extract from the correlation curves is the characteristic decorrelation time, τ^* for both α and β processes. This value follows from fits to the combined $g_1(\tau)$ with the following expression, consisting of two stretched exponential decay functions [7]:

$$g_1(\tau) - 1 = A \exp(\tau/\tau_\beta^*)^\gamma - (1 - A) \exp(\tau/\tau_\alpha^*)^\delta \quad (6.11)$$

This functional form can fit both decays we would expect to see in a glassy sample; β -decay (τ_β^*) and α -decay (τ_α^*). In the case of a sample with only one decay we set A to 1, this eliminates the second term. The characteristic decay time τ^* is not identical to the true decay time (τ) of the sample under investigation. Unlike the relaxation times acquired from dynamical light scattering (DLS) measurements, we need to correct for properties of both the sample under investigation and the measurement setup. The measured decay time of the sample is a function of both the photon transport mean free path, l^* , and the optical path length, L , as $\tau = \tau^*/(l^*/L)^2$. We have no direct knowledge of l^* for all our samples, but we are able to measure it: The ratio between the photon transport mean free path and average light intensity is constant across samples. To exploit this we measure a reference sample for which we do know l^* without changing any experimental settings. Since $I \propto l^*$ this allows us to calculate l^* of our sample of interest via:

$$\frac{\langle I_S \rangle_t}{\langle I_R \rangle_t} = \frac{l_S^*}{l_R^*} \quad (6.12)$$

where $\langle I_S \rangle_t$ and $\langle I_R \rangle_t$ are time averaged intensities measured on the PMT detector for a sample of interest and the reference sample.

Figure 6.8 — Depending on the difference in refractive index between different particle populations and the suspending media we can isolate the scattering signal from a specific population of particles — in this case our signal consists solely of photons scattered by the particles coloured in red.

Contrast variation

We extend the possibilities of MS-DWS with contrast variation. The goal of our experiments is to measure the dynamics of a sample with two distinct particle populations; probe particles mixed at a low concentration with matrix particles. Our interest lies mainly with one of the two populations, the probe particles. Since the scattering intensity scales with the refractive index mismatch between particle and suspending medium, $\Delta n = n_p - n_m$, we can minimise the signal from the

matrix particles by matching their refractive index with the solvent in which they are suspended. In our experiments the matrix particles are PNIPAM microgels below their LCST temperature. In this state they are swollen with solvent, water, and their refractive index is very close to that of the solvent. The resulting Δn is very small. By contrast, our probe particles — polystyrene with a refractive index of ~ 1.6 — differ greatly from the solvent. Therefore, the resulting DWS signal will be dominated by scattering from the probe particles (Fig. 6.8). We can confirm this by measuring l^* for a reference sample and for a sample consisting only of microgels. We measure l^* for a reference sample, $1\ \mu\text{m}$ polystyrene spheres in water at a volume fraction $\phi = 0.01$, by fitting the experimental correlation curves $g_1(\tau)$ for different values of $L = 1, 2$, and $3\ \text{mm}$ — with equation 6.4 (Fig. 6.10). We set the restriction that l^* should be the same for all three samples. With this method we find $l^* = 311\ \mu\text{m}$ for our PS reference sample. With equation 6.12 we are now able to calculate l^* for all our samples by comparing count rates on the PMT detector. The resulting l^* values for all our samples fall within the $0.08\text{--}0.16\ \text{mm}$ range (Fig. 6.9).

Our method is based on the principle of contrast variation, i.e. the probe particles should scatter orders of magnitude more than the matrix particles. A sample of our matrix microgels above ζ_g is optically transparent over a few centimetres by eye. Using the same method as outlined above we also determine l^* for this microgel sample. We find $l^* \sim 2\ \text{m}$; four orders of magnitude higher than our samples with probe particles. Therefore, we conclude that our DWS signal is dominated by the result of scattering by the probe particles.

Figure 6.9 — Values for l^* for all packing fractions and all size ratios as calculated by equation 6.12. Calculated for size ratio $a = 0.2$ (blue squares), 0.37 (green triangles), and 1.44 (red circles). Dotted line at $0.311\ \text{mm}$ indicates l^* of the reference sample.

Figure 6.10 — (A) We extract l^* from the correlation curves of the same sample measured at different optical path lengths, L . (B) A representative decorrelation curve, $g_1(\tau)$ for the secondary cell with a characteristic decay time of $1 \cdot 10^3\ \text{s}$. The solid line is a fit with a compressed exponential decay function. The sample consists of $1.0\ \mu\text{m}$ Polystyrene spheres suspended in glycerol a volume fraction $\phi = 0.01$.

Results & Discussion

For all our samples we measure the correlation curve $g_1(t)$ as a function of matrix packing fraction. We include the point $\zeta = 0.0$ which corresponds to a pure suspension of probe particle with out any matrix microgel particles present, thus measuring the Brownian time scale τ_0 .

The goal of our experiments is to shed light on the dynamical arrest of a binary sized system, where probe particles are dispersed in a matrix of refractive index matched PNIPAM microgels. To this end we probe the dynamics of the system for three different size ratios and a range of packing fractions using MSDWS. We measure systems with size ratios, $a = \frac{r_{probe}}{r_{matrix}}$, $a = 1.44$, $a = 0.2$, and $a = 0.37$. These correspond to the following three scenarios: At $a = 1.44$ the probe particles are larger than the matrix and are a direct measure for the dynamical behaviour of the matrix; we expect the dynamical arrest of the tracers to effectively be a proxy for the behaviour of the matrix particles. As we work at a low PS volume fraction, $\phi = 0.01$, the effects of probe-probe interactions are negligible. At a size ratio $a = 0.2$ the probe particles are very much smaller than the matrix; we would expect there to be two decoupled transitions [17]. Finally when we are at intermediate size ratios, $a = 0.37$, we are left with an open question, do they display behaviour in between the other two extremes or will they tend towards one of the other limiting cases?

We start by measuring the field autocorrelation function $g_1(t)$ for the large probe particles, $a = 1.44$ (Fig. 6.11 C). At lower packing fractions of the matrix, $\zeta = 0.0, 0.14, 0.34, 0.69$ & 0.76 , we observe full and single decay of the correlation functions; the system is in a liquid state. As the packing fraction of the matrix increases, $\zeta = 0.91, 0.92, 0.94, 0.95, 0.96, 1.0, 1.1$ & 1.4 , two decay modes become visible; a β -decay at short times due to cage-rattling and an α -decay at longer times due to particles escaping from their cages. The highest measured matrix packing fraction, $\zeta = 1.4$, there is practically no decay of the correlation function inside the measurement window; at this packing fraction the system is fully vitrified. From these curves we extract the α -decay times for the final decay by fitting to a double stretched exponential function as described in the Materials and Methods section. We plot the resulting structural relaxation time, normalised to the decay time of the measurement at $\zeta = 0.0$, i.e. the sample without any matrix particles present and corrected for $l^*, \tau/\tau_0$ as a function of ζ (Fig. 6.11 D solid red circles). The super-exponential increase in relaxation time as a function of packing fraction can be captured by the the phenomenological Vogel–Fulcher–Tammann (VFT) equation:

$$\frac{\tau}{\tau_0} = \exp \frac{A\zeta}{\zeta_0 - \zeta} \quad (6.13)$$

This equation has seen success in empirically describing the vitrification behaviour of many systems; ranging from colloids [7], to molecular

glasses, to metallic glasses [5]. It captures our results well for $A = 0.7$ and $\zeta_0 = 0.97$, which implies that the system is fully vitrified close to the jamming point at $\zeta = 1$.

Figure 6.11 – Correlation curves $g_1(t)$ for different matrix packing fractions and size ratios. **(A)** For size ratio $a = 0.20$ and matrix packing fraction $\zeta = 0.0, 0.11, 0.28, 0.56, 0.73, 0.84, 0.95$ & 1.12 . **(B)** For size ratio $a = 0.37$ and matrix packing fraction $\zeta = 0.0, 0.11, 0.28, 0.40, 0.56, 0.67, 0.73, 0.84, 0.94, 0.99, 1.05$ & 1.12 . **(C)** For size ratio $a = 1.44$, d matrix packing fraction $\zeta = 0.0, 0.14, 0.34, 0.69, 0.76, 0.91, 0.92, 0.94, 0.95, 0.96, 1.0, 1.1$ & 1.4 . **(D)** Longest-time decay times extracted from correlation curves for size ratios $a = 1.44$ (red solid circles), $a = 0.37$ (green solid triangles), and $a = 0.20$ (blue solid squares). Solid lines are fits to the VFT equation (Equation 6.13).

On the other end of the spectrum is the sample with size ratio $a = 0.2$. The correlation curves show a full decay even for matrix packing fractions higher than unity, where we now know that the matrix particles have formed a glass. This difference becomes immediately obvious with the plot of the extracted characteristic decay times. Whereas for the high size ratio τ increases by 6 orders-of-magnitude, for the small size ratio only a very mild increase of approximately one decade is observed. The dynamics of the small particles is thus only influenced very weakly by the increase in packing fraction of the matrix. Even when $\zeta > 1.0$ we still find a full decorrelation. The weak increase is attributed to a shrinking pore size and thus increasing hydrodynamic coupling, as known for thermal motion in confinement [33].

Diffusing wave spectroscopy in transmission mode is highly sensitive to even small displacements of the scatterers. From equation 6.3 and the fact that $g_1(t)$ will have decayed by a factor $1/e$ after a time $\tau(l^*/L)^2$ we

can find the approximate displacement needed to achieve this amount of decorrelation, Δr_{rms} , via [21]:

$$\Delta r_{rms} = \frac{\sqrt{6} \cdot l^*}{k_0 L} \quad (6.14)$$

$$k_0 = 2\pi/\lambda \quad (6.15)$$

For our systems this evaluates to a displacement of $\Delta r \sim 13$ nm for $g_1(t)$ to decay by a factor $1/e$. This displacement is small compared to the radius of the smallest probe particles, 90 nm.

It would be useful to know our particle sizes and their displacements relate to the interstitial voids as found in the glass. As glasses are a highly irregular material this calculation is not trivial. Therefore, we begin by considering a crystalline close-packed matrix at $\zeta = 0.64$, with which we can calculate the radius of the sphere which fits in the interstitial spaces between the matrix particles. In the case of an fcc crystal we find two distinct interstitial spaces, octahedral and tetrahedral spaces. They differentiate themselves by the number of particles surrounding such interstitial sites. The maximally allowed radius normalised by the radius of the base particles forming the crystal equals: $r_{max} \approx 0.41 r_{base}$. In our case $r_{base} \sim 450$ nm. With a radius of 90 nm the smallest probe particles have ample space to move through the interstitial spaces. If we take into account the facts that at high packing fraction the microgels are likely to compress due to the increased osmotic pressure around them [34, 35] and that our system is most not a fcc crystal but a disordered packing with, on average, larger interstitial sizes as they exist at lower volume fractions; it is no wonder that we observe full decorrelation for all matrix packing fractions with this specific size ratio.

The observed decoupling in the dynamics of the small probe particles and large matrix particles follows the prediction from MCT theory [18, 16], simulations on binary amorphous systems [17], early experimental work [36], and spin-glasses [37]. Therefore, we would expect the small particles to undergo a localisation transition as well at much higher matrix packing fractions. Unfortunately the required packing fractions, $\zeta \gg 1.0$, were unattainable for this experiment. Instead of going to very high packing fractions it should be possible to achieve the same effect by changing the size ratio under study to some intermediate value; with this approach we do not change the pore sizes in the matrix but rather increase the size of the intruders. We expect the resulting effects to be the same.

For this intermediate size ratio we use polystyrene probe particles with a radius of 170 nm; with a resulting size ratio $a = 0.37$, intermediate between 0.2 and 1.44 and below the critical values calculated for an fcc crystal at $a < 0.41$. The correlation curves show the familiar two modal

decay after the matrix packing fraction has increased above its point of dynamical freezing (Fig. 6.11B). In fact, the resulting decay time follows, within experimental error, an identical dependence on ζ as the largest size ratio, $a = 1.44$ (Fig. 6.11D, solid green triangles). From the correlation curves we conclude that for our system this intermediate size ratio behaves the same as the matrix itself; therefore, there is no decoupling in the dynamics of the two species.

Simulation work by Voigtmann et. al. [17] did find separate dynamics at a size ratio of 0.35, which contrasts our findings. Their simulations consisted of 2000 spheres, 1000 small particles and 1000 large particles, all interacting with a truncated Lennard–Jones potential such that only the repulsive part was taken into account. This Weeks–Chandler–Anderson (WCA) potential approximates hard-spheres with a small soft tail [38]. To avoid crystallisation they used spheres with polydisperse radii. The fact that their system consisted of approximate hard-spheres makes direct comparison with our work difficult. The matrix in our system is made of highly deformable and soft microgel particles, which can shrink and facet when needed in response to an increased osmotic pressure [35]; the result of an increase in packing fraction. As matrix microgels shrink, due to osmotic deswelling, the effective size ratio will increase and a possible decoupling is suppressed. To fully answer the question whether there is an intermediate regime present where dynamics decouple at timescales in between the two extremes we have tested, an extensive size ratio series is required.

While the correlation curves of the intermediate and large size ratios shows identical behaviour in their relaxation time this is not necessarily the case as regards the localisation length of the particles trapped in their cages of matrix particles. The localisation length, δ , is comparable to the size of the cage in which the probe particles are located at higher matrix packing fraction beyond their glass transition point. We can access this length scale from the particles mean-squared displacement (MSD); for glassy systems the MSD has a plateau at intermediate time scales. This localisation plateau is the square of a confining length scale which the particle experiences at those times.

Equation 6.4, which describes the correlation function $g_1(t)$ in transmission geometry, is an approximation, valid for $t \ll \tau$, of the full analytic result for this geometry [21]:

$$g_1(t) = \frac{\frac{L/l^*+4/3}{z_0/l^*+2/3} \left\{ \sinh \left(\frac{z_0}{l^*} \sqrt{\frac{6t}{\tau}} \right) + \frac{2}{3} \sqrt{\frac{6t}{\tau}} \cosh \left(\frac{z_0}{l^*} \sqrt{\frac{6t}{\tau}} \right) \right\}}{\left(1 + \frac{8t}{3\tau} \right) \sinh \left(\frac{L}{l^*} \sqrt{\frac{6t}{\tau}} \right) + \frac{4}{3} \sqrt{\frac{6t}{\tau}} \cosh \left(\frac{L}{l^*} \sqrt{\frac{6t}{\tau}} \right)} \quad (6.16)$$

$\sqrt{\frac{6t}{\tau}} = \sqrt{k_0^2 \langle \Delta r^2(t) \rangle}$ via equation 6.3 and $\frac{8t}{3\tau} = \frac{4k_0^2 \langle \Delta r^2(t) \rangle}{9}$. This gives

us access to mean-squared displacement (MSD) curves directly from the DWS data after numerical inversion.

Figure 6.12 – Probe particle mean-squared displacement (MSD), extracted from $g_1(t)$ via equation 6.16. **(A)** MSD curves for system with size ratio, $a = 0.20$ at the same packing fractions as in figure 6.11 A. **(B)** MSD curves for system with size ratio, $a = 0.37$ at the same packing fractions as in figure 6.11 B. **(C)** MSD curves for system with size ratio, $a = 1.44$ at the same packing fractions as in figure 6.11 C. **(D)** Localization lengths, δ for every MSD curve that exhibits a plateau calculated as $\sqrt{\langle r^2(t = 1418s) \rangle}$; indicated by a solid vertical red line in panels B and C. Calculated for size ratio $a = 0.37$ (green triangles) and $a = 1.44$ (red circles). The dashed line is a guide to the eye. The diagonal solid line in panel A, B, and C is a line with a slope of one.

The smallest probe particles show the expected behaviour in their MSD; at very low dilutions their motion is purely diffusive with a slope of unity. As the packing fraction of the matrix increases the dynamics slow down and become sub-diffusive. This can be seen by the slope of the MSD curves on log-log scale which becomes < 1 (Fig. 6.12 A). A full caging plateau however is never reached as was to be expected with a single-mode decay of $g_1(t)$. For the intermediate and largest size ratios (Fig. 6.12 B & C) the situation is markedly different from the small probe particles, but similar between themselves. At low matrix packing fractions there is again only diffusive movement of the probes. However, at higher packing fractions we observe a caging-plateau with an onset around $t = 10^1$ s. In these curves the plateau is preceded by a region with sub-diffusive motion as the particle rattles around in its cage and it experiences hydrodynamic interactions with the cage ‘walls’ [39]. At long time-scales the plateau gives way to a new diffusive regime of α -motion as particles escape from their cages and move around the sample.

From these curves we can extract the localisation length of the probe particles — the cage size experienced by these particles. To this end we take the square root of the MSD value at a set time of 1418 s:

$$\delta = \sqrt{\langle \Delta r^2(t = 1418s) \rangle}$$

For both size ratios which show caging plateaus the trend of δ with matrix ζ follows the exact same trend. This leads us to conclude that not only are the two size ratios identical when it comes to relaxation times, but that, unexpectedly, they feel similar cage dimensions as well. Thus the glass transition is identical for these size ratios. This leads us to conclude that if there is indeed an intermediate regime where the probe particles experience a glass transition after the matrix particles, it should be found at a size ratio $0.20 < a < 0.37$.

Conclusion

With extensive diffusing wave spectroscopy experiments we have tried to shed light on the dynamical behaviour of binary sized colloidal systems. We use contrast variation to probe the dynamics of a single species in the binary mixture. The base matrix consisting of poly-NIPAM microgel spherical particles, which are doped with polystyrene probe particles at several size ratios: $a = 0.20$, $a = 0.37$, and $a = 1.44$. With the largest size ratio we essentially probe the dynamics of the microgel matrix and thus this gives us a baseline. We observe a clear dynamical decoupling between this large ratio and the smallest size ratio. Whereas the large probe particles exhibited the expected two mode decay patterns of a glassy state, we observe no such decay patterns over a similar range in matrix packing fraction. The small probe particles are able to move around in the interstitial spaces between the microgel matrix; their dynamical arrest will occur at microgel packing fractions which we are unable to reach in our experiments. This raises the question whether an intermediate state exists, where the probe particles undergo dynamical arrest after the matrix but before the smallest particles. To this end we measured samples at a size ratio $a = 0.37$. Unfortunately we found no evidence for intermediate behaviour as these particles followed the trends of the matrix, both in relaxation times in $g_1(t)$ and in the localisation length, δ , experienced by the probe particles.

To gain full experimental understanding of the decoupling in dynamics and its features when it comes to the size ratio of a binary system we need to extend our range of measured size ratios and volume fraction. It would be useful to remove the variability of the matrix; here we used

soft microgels which can swell and deform as needed. The use of an index matched hard sphere system would reduce this variability. A recently developed colloidal system which can be index matched and which allows for fine tuning of the colloidal interactions playing a role by tuning the surface chemistry, would be an ideal candidate [40].

The measurements we performed have been limited in time by spurious decorrelations, possibly due to vibrations in the setup. To reduce this effect it would be useful to employ active vibration dampening equipment. Another factor would be a variance in the laser intensity stability and temperature of the setup; especially with temperature sensitive microgels this would be useful. To facilitate the next generation of DWS measurements our lab is currently working on implementing these features such that future measurements on the binary glass transition can be made with higher fidelity and, more importantly, for even further extended time scales.

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APPARENT STRENGTH VERSUS UNIVERSALITY IN GLASSES OF SOFT COMPRESSIBLE COLLOIDS

7

The glass transition in molecular systems can be characterised by the steepness of the growth of a structural relaxation time and temperature. This relation either follows Arrhenius' law, when the liquid is a strong glass former, or displays super-exponential behaviour, a scenario known as a fragile glass. Recently it was postulated that this behaviour could be reproduced in colloidal systems by tuning the particle compressibility. While this hypothesis was supported by experimental data, recent theoretical analysis suggest that this may be an erroneous interpretation. To resolve if and how fragility changes are a real effect in colloidal systems, we employ Monte Carlo simulations. Our simulations confirm the theoretical prediction that the apparent fragility as observed for soft colloids does not map to the molecular world but is due to the use of an extrapolated packing fraction as the control parameter. The experimentally observed changes fragility are not real; they arise only because the relaxation times were plotted against the wrong parameter. Furthermore, our simulation system can be used to explain selective deswelling of substitutional impurities. Even though our simulation model is coarse grained in nature, it can clearly be applied to a wide variety of problems in soft colloidal systems.

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“Apparent strength versus universality in glasses of soft compressible colloids”

In preparation (2018)

Introduction

COLLOIDAL suspensions exhibit a marked slowing down of structural relaxation processes when the volume fraction of particles is increased [1, 2, 3, 4, 5, 6]. In analogy to the dynamical slowing down in molecular glass formers upon quenching the temperature, denoted as a colloidal glass transition. The colloidal glass transition exhibits some striking similarities to its molecular equivalents, such as the emergence of inhomogeneous, collective dynamics [5, 4, 7] and anomalies in the vibrational density-of-states [8, 9, 10]. For hard sphere colloids, interacting solely by volume exclusion, the liquid viscosity grows steeply around a particle volume fraction $\phi = 0.58$, which is identified as the glass transition point ϕ_g , while undergoing a solid-liquid transition at slightly higher packing fractions due to jamming [11, 12, 13, 14, 15]. The steep growth in viscosity around ϕ_g , predicted to diverge according to mode-coupling theory [16], signals the drastic slowing down of structural relaxations over a very small window of volume fractions. Such a steep change in the dynamics with small changes in the experimental control parameter is denoted as a fragile liquid in the colloidal equivalent of the Angell classification of glass fragility [17, 18, 19]. A fragile liquid is characterised by a super-exponential growth of the viscosity with ϕ upon approaching ϕ_g . Seminal experiments on colloidal microgels have suggested that this fragile transition for hard spheres can give way to one in which the growth of viscosity with packing density becomes much more gradual, by increasing the softness of the colloids [20]. For these microgel suspensions it was found that sufficiently soft colloids exhibit a purely exponential growth of relaxation time with ϕ . In analogy to the limiting Arrhenius-scenario in the molecular world [17, 18, 19], these soft colloids were denoted as strong glass formers. This observation triggered the fascinating possibility that the diversity of glass transitions at the molecular scale may be emulated in the colloidal domain with the particle softness as a tuning knob. However, the interpretation of these observations have remained a topic of debate [21, 22].

While the possibility of an analogy between glass fragility in the molecular and colloidal worlds is appealing, it also raises some important yet unanswered questions. Most importantly, since the origins of fragility and strength remain incompletely understood in both molecular and colloidal glasses, mapping one problem onto the other does not necessarily advance our insight. Moreover, since the mechanisms are not fully clear

for both cases, it is also not directly obvious that fragility at both scales is governed by the same physical principles. It may be possible that apparent similarities are in fact the result of very different microscopic physics. Yet, recent publications hint that a universal explanation may be on the horizon; for metallic glasses, it was proposed that the softness of the interatomic potential controls the fragility of the vitrification process [23], while a recent publication of our group has shown a quantitative theoretical approach to explain apparent fragility changes in colloidal glasses based on their compressibility, i.e. softness with respect to deswelling [21]. Focusing on the colloidal domain, which is the aim of this chapter, the previously developed phenomenological mean-field model explores the effect of osmotic deswelling of particles on the perceived changes in dynamics [21]. By accounting for the deswelling of particles in response to the osmotic pressure of the bath, it predicts a strong non-linearity in the relationship between the true volume fraction ϕ and the apparent packing fraction ζ . The latter is the packing fraction the suspension would have if no deswelling takes place and is often the parameter used in experimental studies [20, 24, 25, 26]. As particle deswelling can be severe, ζ can reach values well over unity; as such, its value in describing the free volume in the system is limited. This softness-dependent non-linearity causes changes in the shape of the curve describing the slowing down of the dynamics as a function of the experimental control parameter ζ , with respect to that of the actual parameter that governs the dynamics ϕ . As a consequence, the model suggested that fragility transitions in soft colloidal systems are merely apparent ones due to the use of a control parameter that does not govern the microscopic dynamics in the suspension. The realisation that particle deswelling can cause apparent changes in the steepness of the glass transition was also reached recently after experimental studies on charged microgels [25].

This result provokes the idea that no changes in physics underlie the reported changes in fragility in colloidal systems, but that it is merely an apparent effect due to the lack of knowledge on the real volume fraction of the system at a given particle number density. If this is true, one may argue that softness does not break the universality of the slowing down of relaxations with the appropriate state variable ϕ and a link with molecular fragility is lost. To resolve this issue, new methods are required in which no essential features of the system, such as a universal slowing down with ϕ , have to be assumed a-priori. Unfortunately, our previous analytic theory relied on exactly this assumption [21], and the validity of the hypothesis above cannot be tested based on the results of this theory alone. Ideally, we would be able to explore the validity of observed fragility changes in soft colloidal systems without the necessity of making such simplifications.

In addition to the uncertainty of the microscopic mechanisms that

control fragility transitions, it also remains unclear what is the connection between the fragility of a liquid and its propensity to exhibit dynamical inhomogeneities. Dynamical heterogeneities are a characteristic hallmark of the glass transition [7, 4], where the glass exhibits small pockets of a few to hundreds of particles, of which the local mobility differs significantly from that of the ensemble mean. For molecular glass-formers, it is common to presume that the fragility of the glass transition is intimately linked to the emergence of cooperative motion, leading to inhomogeneous dynamics [27, 28]. However, the validity of this argument remains under debate [29], as does the causality of these two features. For colloidal systems, no in-depth exploration exists that unambiguously connects the fragility of the glass transition and the emergence of clusters of cooperatively moving particles. However, experiments reveal a hint that such a connection may exist. A comparison between the behaviour of glasses formed from soft microgels versus incompressible hard spheres, which exhibit strong and fragile glass transitions, respectively, as evidenced in other publications, seem to indicate that the glass of soft particles shows significantly more homogeneous dynamics as compared to their incompressible counterpart [30]. If the link between fragility and dynamical heterogeneity persists up to the colloidal scale, it could enable an in-depth study of the causality of this connection.

In this chapter we employ a dynamical Monte Carlo simulation model to explore fragility transitions in two-dimensional glasses formed from soft and compressible spheres. We show how the previously postulated in analytical theory and experiment fragility changes with particle compressibility can be recovered, without requiring the assumption of a universal slowing down or a fixed equation-of-state. Our results show how liquids of soft colloids exhibit apparent fragility transitions in the parameter ζ , but when the data is replotted against the true volume fraction ϕ , a universal master curve is obtained, which is independent of softness. This implies that fragility changes with particle softness in colloidal systems are only apparent ones, which do not involve any changes in the microscopic physics of the system. This is further supported by the fact that also the extent of dynamical heterogeneities can be collapsed using the true volume fraction as the state variable. Finally, we illustrate how the simulation method we develop here to account for particle deswelling, can also be used to explore other remarkable features found in soft suspensions, such as the selective deswelling of impurities in colloidal crystals due to a softness mismatch.

Particle compressibility in dynamic MC

To explore the effects of particle compressibility without requiring a-priori assumptions regarding the equation-of-state and the kinetic master curve, as required in our previous theoretical efforts, we employ a dynamical Monte Carlo model in which these effects emerge from a minimal model. We study vitrification in a two-dimensional system of bidisperse discs composed of $N = 2000$ discs of initial radii $a_{0,L} = 0.7 \sigma$ and $a_{0,S} = 0.5 \sigma$, at a 1:1 number ratio, in a square box with periodic boundaries. To parameterise the model, we start from the conventional approach to simulate soft spheres, which is a simple power-law contact potential:

$$U_{ij}(r) = \epsilon \left(\frac{a_i + a_j}{r} \right)^6 \quad (7.1)$$

in which ϵ is the overlap energy at particle contact. While such a soft-sphere potential has been used to explore a wide variety of effects in soft sphere systems, such as vitrification and crystallisation [31, 32], it does not capture the particle compressibility. If particles are highly compressible, the sizes $a_{i,j}$ are no longer constants and will depend on the particle concentration and the local packing structure. Such osmotic deswelling has been extensively evidenced in experimental systems, for example microgel colloids or star polymers [33, 34].

To introduce compressibility of the particles into the Monte Carlo model, we consider the free energy of isotropic particle compression for soft compressible spheres swollen with a solvent, e.g. microgels or star polymers. Volume changes are described by the swelling ratio $\alpha_i = a_i/a_{0,i}$, where $a_{0,i}$ is the equilibrium swollen radius of particle i in the dilute limit where osmotic forces are negligible. For the sake of simplicity, we presume that the (de-)swelling energy W is parabolic around its minimum at $a_{0,i}$ for small changes in particle size. However, in reality particles exhibit a finite compressibility; upon strong compression, all solvent is expelled from the polymeric objects and the particle compressibility effectively vanishes. To capture these effects we use a finite-compressibility parabolic form:

$$W_i = \frac{\kappa(1 - \alpha_i)^2}{\frac{\alpha_i}{\alpha_c} - 1} \quad (7.2)$$

in which α_c sets the limiting degree of deswelling where the particle expels all solvent and becomes incompressible. The energy scale κ controls the compressibility of the particles, and is thus the softness parameter in this study.

For each Monte Carlo trial move, we either translate a randomly selected particle by some small distance δr , drawn from a Gaussian distribution with a zero mean and a width proportional to $1/a_i$ [35], or we perform a move in which the size of a randomly selected particle is updated $a_i(t) = a_i(t - \delta t) + \delta a$, in which $\delta a \ll a_0$. The effective time t^* in the simulations is normalised to the acceptance rate of translation moves in accord with previous studies [35, 36]. Translation and (de)compression moves are rejected or accepted by evaluating the Boltzmann probability of the total energy defined as:

$$E = \sum_i^N \sum_j^N U_{ij} + \sum_i^N W_i \quad (7.3)$$

In this way, structural relaxation by translation *and* osmotic (de-)swelling, both occurring in systems of compressible particles, can be accounted for on a coarse-grained level.

It is our aim here to explore how compressibility affects the nature of the slowing down of relaxations in fluids of soft colloids. To this end, we choose a constant value of the contact energy $\epsilon/k_B T = 5$ and collapsed particle size $\alpha_c = 0.25$ and vary the compressibility constant κ . In some sense, this is equivalent to varying the Poisson's ratio ν of the particles; for $\kappa = \infty$, the particles are incompressible ($\nu = 0.5$), e.g. describing emulsion droplets, while finite values of κ give a phenomenological description of compressible particles, $\nu < 0.5$ such as microgel colloids or star polymers.

In our previous analytical theory we proposed that the origin of fragility transitions lie in the fact that osmotic deswelling of soft particles causes a non-linear relationship between the real volume fraction and the extrapolated volume fraction [21]. In this chapter we study the glass transition of soft colloids in two dimensions and define the real area fraction as:

$$\phi = \frac{\pi}{A} \sum_i^N a_i^2 \quad (7.4)$$

where $A = L^2$ is the area of the square simulation box. Since in experiments it is often not possible to obtain the size of each particle at the relevant volume fractions, many researchers make use of an extrapolated packing fraction that is defined as:

$$\zeta = \frac{\pi}{A} \sum_i^N a_{i,0}^2 \quad (7.5)$$

which presumes that the particles retain their original size irrespective of the particle concentration. This is valid for incompressible spheres where

$\phi \equiv \zeta$, but fails for soft particles as these can exhibit pronounced deswelling so that $\phi < \zeta$. In fact, deswelling can be so strong that if the particles are sufficiently soft and the osmotic pressure sufficiently high, the glass transition is moved from $\phi_g = 0.58$ for hard spheres to effective packing fractions $\zeta \gg 1$.

Results & Discussion

Accounting for osmotic deswelling has a pronounced effect on the properties of the simulated colloidal glasses. The fact that osmotic deswelling is relevant in experimental systems, in particular for microgels and star polymers, has been confirmed extensively in previous studies, both experimentally [37, 38, 26, 39, 33, 40, 41, 42, 43, 44, 45, 25] and theoretically [46, 47, 48]. Here we account for compressibility to first order by introducing an energy associated with deswelling, which takes the form of a quadratic finite-compressibility equation for each particle. We note that we have previously shown using analytical theory [21] that the exact shape of the osmotic deswelling curve with respect to the particle density does not change the underlying physics, but only the absolute values of the packing fraction where deviations from the incompressible case occur. As it is our aim here to explore the concept of how particle compressibility affects fragility and dynamical heterogeneity in colloidal glasses, we use this simple form. However, our simulation approach can be readily adapted to different forms for the osmotic energy W , e.g. to describe a specific system in more microscopic detail.

We first explore how particle compressibility influences the size distribution of particles in the glass as a function of packing fraction. For rigid and largely incompressible particles, $\kappa/k_B T = 5 \cdot 10^4$, we find, as expected, that the bidisperse population remains bidisperse even at high concentrations (Fig. 7.1A) and that the distribution of relative deswelling degrees $P(a/a_0)$ is sharply peaked at 1 (Fig. 7.1D, G & J), indicative of little to no osmotic volume regulation up to the highest density explored here.

Making the particles more compressible significantly changes this behaviour, and leads to volume adaptation of the particles as the particle packing fraction is increased. Both for intermediate and high compressibilities, $\kappa/k_B T = 500$ (Fig. 7.1B) and $\kappa/k_B T = 50$ (Fig. 7.1C), we observe a strong growth of the polydispersity induced by osmotic deswelling. This is visible in the renderings of the simulation box (Fig. 7.1B–C) and in the deswelling distributions (Fig. 7.1E–F, H–I & K–L). Not only does the average particle size shrink as the density is increased, visible as a shift of the mean a/a_0 to lower values, we also observe a distinct broadening of the

Figure 7.1 – **A–C)** Visual representation of two-dimensional glasses of compressible particles where the particles are colour-coded according to their relative deswelling ratio a/a_0 as indicated by the colour bar, for $\kappa/k_B T = 50000$ and $\zeta/\zeta_g = 0.59$ (**A**), $\kappa/k_B T = 500$ and $\zeta/\zeta_g = 0.58$ (**B**) and $\kappa/k_B T = 50$ and $\zeta/\zeta_g = 0.59$ (**C**). **(D–L)** Distribution of relative particle sizes, illustrating the extent of osmotic deswelling as a function of compressibility scale κ for $\kappa/k_B T = 50000$ and $\zeta/\zeta_g = 0.59$ (**D**), 0.23 (**G**), 0.10 (**J**), $\kappa/k_B T = 500$ and $\zeta/\zeta_g = 0.58$ (**E**), 0.23 (**H**), 0.06 (**K**) and $\kappa/k_B T = 50$ and $\zeta/\zeta_g = 0.59$ (**F**), 0.23 (**I**), 0.1 (**L**).

distributions. Since the glass offers a heterogeneous micro-environment for each particle, due to the disordered structure, the local pressure each particle experiences is also inhomogeneous with a broad distribution of deswelling degrees as a result. This can be most clearly seen in the case of the very compressible particles ($\kappa/k_B T = 50$, Fig. 7.1C). In all cases, we find that the initially bidisperse system remains in a glassy state, with no signs of medium- or long-ranged crystalline order, as evident from a liquid like pair-correlation function $g(r)$ (Fig. 7.2A).

These observations of strong local volume regulation in a system of size mismatched compressible particles is in direct agreement with seminal experiments by the groups of Lyon and Fernandez-Nieves; they showed that a single large and soft microgel can exhibit severe deswelling to fit into a crystalline lattice of smaller particles [38, 49, 37]. In the final section of this chapter, we will show that our simulation model can in fact reproduce these specific observations.

Apparent fragility

We proceed to explore the effects of this concentration-dependent osmotic deswelling, regulated by the compressibility energy scale κ , in the slowing down of structural relaxations. To do so, we compute the self-intermediate scattering function from our simulation data as $F_s(q, t) = \langle \exp(i\mathbf{q} \cdot [\mathbf{r}(t) - \mathbf{r}(0)]) \rangle$ where we choose $q = 2\pi/a$ as the scattering vector to probe particle self-diffusion, where a is the ensemble-mean particle

Figure 7.2 – (A) Radial distribution function, $g(r)$, calculated for simulation snapshots at $\zeta = 1.15$ for $\kappa/k_B T = 50, 500, 5000$, & 50000 (down triangles, circles, up triangles, squares) (B) Kinetic fragility index m as a function of osmotic deswelling energy κ , dotted line at $m = 5$ gives the limiting fragility for a purely strong glass, dotted line at $m = 38$ that for the most fragile glass in these simulations. (C) Self-intermediate scattering functions $F_s(q, t)$ from simulations (symbols) and fitted as described in the text (lines) for $q = 5.2 \mu\text{m}^{-1}$, $\kappa/k_B T = 50000$ and $\zeta =$ (from left to right) 0.0581, 0.103, 0.149, 0.192, 0.232, 0.258, 0.287, 0.322, 0.363, 0.413, 0.474, 0.534, 0.568, 0.605, 0.646, 0.769, 0.860, 0.930 & 1.010. (D) Terminal structural relaxation time τ as a function of the effective packing fraction ζ and (E) the same data in an Angell representation, where ζ_g is defined as the condition where $\log(\tau/\tau_0) = 5$. We have calculated this for systems with $\kappa/k_B T = 5$ (purple left triangles), 50 (red down triangles), 500 (blue spheres), 5000 (orange up triangles), and 50000 (green squares) (F) The same data plotted as a function of ϕ , as calculated according to equation 7.4.

size for that particular simulation run. The shape of the self-intermediate scattering functions (Fig.7.2A) is very similar to those found for two-dimensional colloidal glasses of soft particles, both in experiments [50] and in simulations [51], with a characteristic terminal decay that shifts to larger times as the concentration is increased, reflecting the slowing down of structural relaxations.

While the $F_s(q, t)$ curves do not show a clear separation between a short time and a long time decay, typically interpreted as a fast cage rattling and slow cage breaking motion, we find that they cannot be fitted by a single stretched exponential decay but are described well by a double exponential decay (solid lines in Fig.7.2A), indicating that these two modes of relaxation are still present. The smoothing of the two decays

into a quasi-continuous and strongly stretched decay may be the result of the long-wavelength fluctuations that exist in two-dimensions. Whether these effects alter the physics of the liquid-solid transition as a function of the dimensionality of the system, is a recent topic of debate [51, 50, 52, 53] and is outside the scope of this chapter.

For incompressible particles, $\kappa/k_B T = 50000$, the characteristic long-time structural relaxation time τ , normalised to that for freely diffusing particles at very low densities τ_0 , shows a steep growth at an effective area fraction $\zeta = 0.8$ (Fig. 7.2D, green squares), in accord with experiments [50]. By contrast, lowering the particle compressibility leads to a much more gradual growth of the relaxation time (Fig. 7.2D red down-pointing triangles). We observe how values of the effective packing fraction ζ well above unity are required to realise a significant slowing down of the dynamics; this is in direct agreement with experimental observations on suspensions of soft and compressible spheres [20]. For the softest particles, $\kappa/k_B T = 5$, the relaxation times start to deviate and are generally untrustworthy. With these soft particles the compressed simulation box is so small that finite size effects start to play a major role. We show the data in figure 7.2 but do not consider it for further analysis.

To define a glass transition point ζ_g , we follow the approach employed previously by other authors [11, 54], as the packing fraction where $\tau/\tau_0 \equiv 10^5$. While this definition is somewhat arbitrary by definition, a similar criterion is used in the study of fragility in molecular glasses, as first proposed by Angell [19]. By direct analogy, we can construct a so-called Angell plot of our simulation data in which we plot the relative growth of τ as a function of the scaled packing fraction ζ/ζ_g .

Indeed we find that this gives rise to apparent changes in the fragility of the colloidal glass transition. Whereas the incompressible spheres exhibit a fragile vitrification, the strength of the glass transition increases as κ decreases. Interestingly, this result required no a-priori assumption of the shape of the dynamical slowing down nor on the equation-of-state of the suspension, while this was required in our previous analytical theory. This confirms the validity of our theoretical argument explaining how particle compressibility governs the apparent fragility of the colloidal glass transition. This becomes even more clear when we quantify the apparent fragility of the glass transition using the kinetic fragility index, defined for colloidal systems as:

$$m = \left. \frac{d \log(\tau/\tau_0)}{d(\zeta/\zeta_g)} \right|_{\zeta=\zeta_g} \quad (7.6)$$

which has a limiting value for a strong glass $m \equiv 5$, dictated by our definition of the point of vitrification as $\log(\tau/\tau_0) = 5$ and grows as the glass transition becomes increasingly fragile. In validation of our theoretical

result, we find that m is directly controlled by the particle compressibility κ (Fig.7.2B). Moreover, the values of the fragility index m are in direct agreement with our previous theoretical study

We have now shown how these coarse-grained simulations capture some of the essential features previously found in experiments [20] and in analytical theory [21]. However, as speculated in the introduction, the observed fragility changes may only be apparent ones that arise from the use of an extrapolated packing fraction, which is strongly non-linear in the true volume fraction ϕ . If this is true, all the curves of τ/τ_0 should collapse when plotted against ϕ , which accounts for the actual deswelling ratio of the particles and thus is a measure for the real free volume in the suspension. Indeed, we find that all of the simulation data, from very hard and incompressible spheres to the most compressible ones explored here, can be collapsed simply by exchanging the state variable ζ for the true volume fraction ϕ (Fig.7.2F). This not only confirms that the assumption of dynamical universality in ϕ in our previous analytical theory was correct [21] but that the apparent fragility changes in soft colloidal systems are not associated with a change in microscopic physics.

Softness and inhomogeneous dynamics

So far, we have used our minimal simulation model, which accounts at a coarse-grained level for osmotic regulation and particle deswelling, to validate our analytical theory proposed previously and to illustrate the origin of apparent fragility changes in colloidal glasses of soft particles. Recent experiments of Rahmani et al. [30] have hinted that in addition to changing the apparent glass fragility, particle softness also has a marked effect on the emergence of dynamical inhomogeneities. This is an interesting observation since fragility transitions and the propensity of systems to exhibit inhomogeneous local dynamics have also been linked for molecular and atomic glasses [55, 56]. We can thus ask if our simulations give rise to similar observations.

To explore the homogeneity of the dynamics in our simulation model, we use the standard approach often employed for colloidal glasses. First, we compute the displacement probability distribution $P(\Delta x(t))$ from our simulations. Both for the soft and hard particles we observe how the step size distribution is relatively Gaussian at small value of t , while larger values of t give rise to a distribution with exponential tails at large displacements (Fig.7.3A–B). The exponential tails are the signature of a wide distribution of local mobilities, a characteristic fingerprint of the glassy state, and have been observed also in experiments on colloidal glasses [57, 4]. Using this metric, we can compute the non-Gaussianity of the displacement distributions as the ratio of the fourth and second

Figure 7.3 – Displacement probability distribution $P(\Delta x)$ from our simulations. For soft particles, $\kappa/k_B T = 50$, (A) and incompressible particles, $\kappa/k_B T = 50000$, (B) (C) Non-Gaussian parameter β_2 for soft particles, $\kappa/k_B T = 50$ and (D) for incompressible particles, $\kappa/k_B T = 50000$. As a function of lag time t for a wide variety of packing fractions (red = low, blue = high), (E) Maximum value of the non-Gaussian parameter $\beta_2^{\max}$ as a function of the extrapolated packing fraction ζ . We have calculated this for systems with $\kappa/k_B T = 50$ (red down triangles), 500 (blue spheres), 5000 (orange up triangles), and 50000 (green squares) (F) Same data as (E), but plotted as a function of the true volume fraction ϕ .

moments:

$$\beta_2(t) = \frac{\langle \Delta x^4 \rangle}{3\langle \Delta x^2 \rangle^2} - 1 \quad (7.7)$$

which for a purely Gaussian distribution $\beta_2 = 0$. Our system is polydisperse by design and we have chosen to use a particle-size dependent MC step size, as prescribed by the Stokes–Einstein relation. As an effect, the non-Gaussian parameter β_2 does not reach its expected zero value at the shortest times. Our particles undergo non-Gaussian displacements even at these short times because of the emergence of multiple populations as a result of deswelling.

When we plot β_2 as a function of the correlation time t (Fig.7.3C–D) we find curves that exhibit a very similar trend as observed previously in experiments, both for two- and three-dimensional colloidal glasses. At low volume fractions, the dynamics are very homogeneous and no

Figure 7.4 – Left: Osmotically-induced particle size fluctuations as a function of time, for $\kappa/k_B T = 50$ (red triangles), $\kappa/k_B T = 500$ (blue circles), and $\kappa/k_B T = 50000$ (green squares). Right: corresponding probability distributions $P(a)$ of the size of a single particle over time, which reveal a Gaussian shape. All samples are at $\zeta = 0.93$.

significant heterogeneity is observed. As the volume fraction is increased and the glass transition point is approached, dynamical heterogeneity emerges as a distinct peak in $\beta_2(t)$. The peak height β_2^{max} can be taken as a proxy for the extent to which the dynamics are inhomogeneous. Plotting these data against the extrapolated packing fraction again appears to indicate differences between hard and soft particles, with much lower values of β_2^{max} for a given value of the packing fraction ζ for the hard particles (Fig.7.3E). However, also here we can ask if these differences are artificial due to the fact that the system dynamics are governed by the true volume fraction. Re-plotting β_2^{max} as a function of ϕ reduces the differences between the different softnesses to a large extent (Fig.7.3F). This suggests that, in analogy to the fragility, also changes in the amplitude of dynamical heterogeneities vanish when the appropriate state variable ϕ is used. We note that in this case plotting the data as a function of ϕ reduces the difference between the curves to a large extent but does not collapse the data sets perfectly. In particular for the softest particles, we find stronger non-Gaussian displacements at lower volume fractions as compared to their incompressible counterparts. This may be due to the fact that the softest particles show the largest extent of osmotic deswelling, which leads to a strong increase in the polydispersity of the suspension as shown above in Fig.7.1. If the particle size fluctuates significantly under conditions of strong osmotic regulation, i.e. small values of κ and high volume fractions ϕ , the time-averaged value of the particle size a_i that we use to account for polydispersity in computing $P(\Delta x)$ may not be able to fully correct for particle size disparity.

To highlight this effect, we plot the temporal fluctuations in the size of a single particle $a(t)$. As the glass is dynamic, the local micro-environment a particle experiences fluctuates in time, leading to changes in the local osmotic pressure. For hard particles, whose size is relatively independent of the local pressure, the size is thus also constant in time with only minor fluctuations (green square symbols in Fig. 7.4). By contrast, for softer particles, the fluctuations in the micro-environment

Figure 7.5 – Snapshot from the simulations with the particles colour coded according to their a/a_0 , with their displacements $\delta\vec{r}$ over a time interval equal to the lag-time of β_2^{max} projected as a scaled red line, for **(A)**: $\kappa/k_B T = 50$, $\zeta = 0.93$, and $dt^* = 71$ at $1.5 \times$ original displacements **(B)**: $\kappa/k_B T = 500$, $\zeta = 0.93$, and $dt^* = 529$ at $1.5 \times$ original displacements **(C)**: $\kappa/k_B T = 50000$, $\zeta = 0.93$, and $dt^* = 4180$ at $2.5 \times$ original displacements.

lead to strong size fluctuations (blue circle and red triangle symbols in Fig. 7.4). We also note that the distribution $P(a)$ of temporal size fluctuations is Gaussian in all cases (right panel Fig. 7.4). Due to the large fluctuations for the softest particles, correcting for these by a time-average value of $\langle\alpha_i\rangle$ to obtain the size-corrected displacements Δx_i is thus only a first order correction and presumably leads to the small deviations in the collapse of the curves of the dynamical heterogeneity versus true volume fraction ϕ (Fig. 7.3F). On the basis of these data we thus conclude that the imperfect collapse of the data in Figure 7.3F is not due to real changes in the nature of dynamical inhomogeneities.

Finally, we confirm this by inspecting the spatial configuration of particle displacements under conditions where dynamical inhomogeneities are significant. We reconstruct our simulation box at a given point in time by colour-coding the particles according to their relative size, a/a_0 , and superimposing their instantaneous displacement vector $\delta\vec{r}$ over a time interval dt^* equal to the time at which we find the maximum in β_2 (Fig. 7.5); we observe that in all cases, from the hard to the softest particles, pockets of correlated particle motion emerge, whereas large parts of the colloidal glass have remained relatively immobile. Also here, no significant differences are observed going from incompressible to soft particles.

These data thus imply that both the changes in fragility and the changes in dynamical inhomogeneity as a function of softness that have been observed in experiments [20, 30] are only apparent ones that result from the overestimation of the packing fraction when using ζ rather than ϕ as the experimental control parameter.

Crystals and selective deswelling

Above we have shown how our minimal simulation model can account for the softness-dependent osmotic deswelling of compressible colloids in dense suspensions and how this may lead to apparent changes in the microscopic properties of colloidal glasses made from these particles. The effect of softness in colloidal suspensions extends far beyond the realm of disordered glasses and has a pronounced effect on a wide variety of phenomena, including crystallisation and supramolecular self-assembly. Our simulation model can be readily extended to explore how deswelling influences these scenarios as well.

As a proof-of-principle we consider the crystallisation of monodisperse microgel particles in which a small fraction of larger impurities is introduced. This scenario was explored both when both particle species are of equal stiffness [58] and in cases where the larger impurities were effectively softer, e.g. due a crosslinking gradient [38, 49, 37]. In both cases, the size ratio of small to large particles in their swollen state was ≈ 0.6 – 0.7 . In the first case, it was found that a small amount of impurities can be accommodated by the crystal lattice of the smaller particles by creating a substitutional vacancy defect, whereas impurities above a certain threshold concentration created a bidisperse glass [58]. In the second case, a selective deswelling of the softer large particles was observed. In this scenario, the osmotic energy penalty for selectively deswelling the large particle is apparently balanced by the energy gain through reduction of lattice strains in the crystal. It was recently shown that the selective deswelling of larger particles in a sea of smaller ones can be explained on the basis of the overlap of the diffuse cloud of counter ions at high enough packing densities in charged suspensions [49, 37]. By adapting our approach to the case of a large impurity in a crystal of smaller ones, we will show here that a softness mismatch of sufficient strength, between impurity and matrix particles, is sufficient to achieve selective deswelling and obtain a defect-free crystal despite the size disparity.

We initialise our simulation model by creating a two-dimensional crystalline configuration of monodisperse particles of $a_{S,0} = 0.5 \sigma$. We introduce a single substitutional impurity by replacing one particle with a large impurity with $a_{L,0} = 0.71 \sigma$, which gives a size ratio of 0.7 . The small matrix particles have a fixed compressibility energy of $\kappa/k_B T = 5000$. If we introduce a substitutional impurity with the same compressibility as the matrix, $\kappa_i/k_B T = 5000$, we find that the impurity distorts the surrounding crystal lattice and causes the proliferation of defects (Fig. 7.6A). We visualise this effect via a time-averaged positional map, colour coded according to the two-dimensional order parameter, $\psi_{6,i} = n_c^{-1} \sum_{j=1}^{n_c} \exp[i6\theta(r_{ij})]$, where n_c is the number of neighbours of particle i over which the sum runs.

Figure 7.6 – Left: Probability distributions $P(a)$ of the size of a single particle over time for a particle in the crystalline matrix far away from the intruder (red circles) and for the intruder (blue triangles). Calculated from simulations with $\kappa_i/k_B T = 5000$ (**A**; equal to the matrix) and $\kappa_i/k_B T = 500$ (**B**; weaker than the matrix). Right: corresponding ψ_6 maps, calculated over the average of 1000 consecutive simulation snapshots. The maps show a small fraction of the simulation box ($N = 2025$) centred around the intruder particle depicted in red. All samples are hexagonal close-packed at initiation of the simulation.

Clearly, introducing multiple of such impurities would result in a loss of crystal symmetry and result in a bidisperse glass at sufficient impurity levels. This is in accord with experimental findings [58]. However, if we make the impurity significantly softer than the surrounding matrix, $\kappa_i = 500$, we observe that it indeed deswells selectively, reducing the number of defects and the spatial extent of the ‘damage’ zone, until for the softest impurity it accommodates fully to the lattice, resulting in a defect-free crystal (Fig. 7.6B). These results suggest that impurities of identical compressibility to the matrix will form glasses at sufficient packing density [58], while a compressibility mismatch can result in selective deswelling with the crystalline order retained despite the difference in the fully swollen size [49, 37].

Due to the method by which microgel colloids are typically prepared, resulting in a radial gradient in crosslinking density from the particle core to its periphery [59], larger particles are somewhat softer than smaller ones when prepared with identical initial crosslinker to monomer ratio. As a result, even in polydisperse microgel suspensions prepared in the same pot, this selective deswelling may reduce the particle size dispersity at high packing fractions, thus allowing such compressible particles to crystallise at higher initial polydispersity as compared to hard and incompressible spheres, where high monodispersity is required to form defect free crystalline structures [60].

Conclusion

We have shown how particle size regulation can be taken into account in a dynamical Monte Carlo model for soft and compressible colloids. This enables the study of osmotic deswelling in dense suspensions. We find that for colloidal glasses of compressible colloids apparent changes in the liquid fragility and dynamical heterogeneity emerge due to the use of an extrapolated packing fraction as the control parameter, while the dynamics are universal when plotted as a function of the true volume fraction, which takes the deswelling into account. This suggests that colloidal glasses of soft particles are always fragile when the appropriate state variable is used. Moreover, we show how the same method can be used to explain the selective deswelling of a substitutional impurity in a colloidal crystal of microgel particles. While coarse-grained in nature, our method enables the efficient simulation of the effects of osmotic deswelling in dense systems of soft and solvent-swollen colloids. In this chapter we have explored the effect this has on phase transitions in purely repulsive systems, but in principle the method can be readily adapted to also explore the effects of volume regulation on the self-assembly of soft colloids either driven by external fields [61, 62] or by means of supra-molecular interactions [63, 64, 65].

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TOWARDS COLLOIDAL FRET SENSORS TO VISUALISE AND MEASURE INTERPARTICLE FORCES

8

The fundamental principle governing a material's response to stresses is the distribution of forces inside the material down to its primary building blocks. While several methods exist for soft matter systems to analyse the dynamical behaviour of its constituent components, we lack a method to measure and map the distribution of forces in a soft material. In this chapter we aim to take the first steps towards such a sensor for colloidal systems. With the design goals of force mapping and quantitative measuring in mind we design the principle for a self-reporting colloid based on FRET force sensors. The final design of the sensor colloid should be capable of reporting contact forces acting upon it via a grey-scale increase in FRET efficiency with increasing forces. While we do not reach our goal here, we lay the foundations for the colloidal sensor with experiments supplemented by simulations. This combination of methods allows us to define a future approach to realise this self-reporting soft matter sensor system.

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Introduction

PROPERTIES of materials fundamentally depend on interaction forces between the components of the material. This is also the case for soft materials. For a colloidal gel, the attractive forces between the colloids allow the material to resist deformation and form a solid [1]. The introduction of even a small force can already fully change the phase behaviour of some materials. For example, the introduction of a small attractive force in an otherwise fully repulsive amorphous colloidal glass, gives rise to re-entrant melting and a liquid pocket in its phase diagram [2].

The distribution of forces in a material under stress is the main determining factor of its mechanical response. For ordered materials, such as crystals, this distribution can be understood based on the underlying crystal structure. Because of the regularity of this structure, the forces are redistributed along the crystal planes [3]. A more complicated case are disordered materials, which virtually all soft solids are. The lack of symmetry makes force distribution a complex and statistical problem. For disordered materials it is well known that the internal thermal dynamics are strongly heterogeneous; the magnitude of Brownian motion of particles in one part of the material is not the same as that in another place. In fact, distinct regions of high and low dynamics have been observed in many systems [4, 5]. However, the connection between these areas of high and low dynamics and the question how mechanical forces are redistributed remains poorly explored. A lack of insight between the mechanics at the smallest scale and those observed macroscopically prevents the development of predictive models for soft mechanics. While most materials are thermal, that is to say they have internal dynamics such as Brownian motion driven purely by a finite temperature, a different class of materials exists where this is not the case — such as sand. The mechanical response of these athermal materials is fully driven by contact forces such as friction. Observation of these contact forces in disordered athermal materials revealed the presence of a distinct network of force-bearing contacts, the so-called force-chain network. Instead of every particle participating in the transduction of forces, only a small percentage do and those form a highly branched network throughout the material. With the help of birefringent particles these force network have been beautifully visualised [6]. However, their possible equivalent in thermal systems remains as of yet obfuscated. We need new methods to measure and visualise the distribution of forces in thermal colloidal

materials, preferably at high speeds and in three dimensions.

If we want to elucidate how force distributions inside materials lead to macroscopic responses we need methods capable of measuring the tiny forces at play at the colloidal length and time scale. Current methods for measuring forces between colloids are based on atomic force microscopy (AFM) [7, 8] and optical, or acoustic, tweezers [9, 10, 11]. While these techniques can measure truly tiny forces on the order of several pN to even fN [12, 13], they are not suitable for measurement of forces inside packings as they are mainly suited to measure forces acting between pairs, or a small amount, of particles. These methods become useless when we want to measure forces deep inside packings of particles. Different force sensing methods are based on optical effects. A suspension of para-magnetic colloids will align when placed in a magnetic field. By measuring the position of the Bragg diffraction peak of the suspension at various field strength one can get the full force-distance relationship of the particles under study [14]. While this method has some clear limitations, mainly in the need for para-magnetic particles, the idea of using optical effects to study colloidal forces has recently led to some interesting developments.

Instead of Bragg diffraction this new generation of sensors uses the fluorescence of the probe, a conjugated polymer, as a signal from which small forces can be deduced. These polymers behave in analogy to spring based scales on a macroscopic level. The polymer acts as an entropic spring; a free polymer in solution will assume an overall size with as many possible realisations as possible, maximising entropy. To either compress or elongate the polymer we need to apply a force. Forces acting upon either a macroscopic or entropic polymer spring can elongate or compress the spring and in the case of conjugated polymers we can translate this change in conformation into an optical signal with the use of Förster resonance energy transfer FRET.

The new generation of molecular self-reporting force sensors uses direct spectroscopic characteristics of their fluorescence emission or combines the idea of an entropic spring with FRET. FRET uses the transfer of an excited state in a donor molecule to an acceptor molecule via dipole-dipole resonances and without the re-emittance and acceptance of an actual photon. The time-averaged efficiency of this transfer process, E_F , is highly dependant on the distance between donor and acceptor moieties, r_{da} , as $E_F \propto \frac{1}{1+r_{da}^6}$ [15] (Fig. 8.1). This effect is exploited by a conjugated polymer whose backbone is almost entirely made out of donor monomers with the occasional acceptor in between. The difference in polymer spring configuration changes the average distance between donors and acceptors and thus changes the FRET efficiency. These next generation single-molecule self reporting force sensors have

Figure 8.1 – Schematic overview of Förster resonance energy transfer (FRET). An electron on the donor molecule which has been brought to its excitation state, $S_0 \rightarrow S_1$, has several pathways to decay back to its ground state. One of those, fluorescence, happens via the emission of a photon (**left hand side**, thick green arrow). However, if there is a compatible acceptor molecule close by, there is the possibility of an additional decay pathway whereby the excited states non-radiatively transfers from donor to acceptor molecule. If the now excited acceptor relaxes via photon emission, we would observe a photon of a lower wavelength as that we would expect for donor emission. This efficiency of this non-radiative pathway is strongly dependent on the distance between donor and acceptor and their dipole alignments. A distance equal to the Förster radius has, by definition, an efficiency of 0.5, $E_F(r = R_F) \equiv 0.5$. For separation distances much higher than R_F there is no FRET (**left hand side**), while for distances within nanometers of R_F there can be FRET (**right hand side**).

so far been successfully used to study the templated-self assembly of custom designed proteins and the forces needed to stretch polymers on a single molecule level[16, 17, 18].

Here we work towards extending the functionality of the FRET polymer force sensors and apply them to both measure and visualise forces in colloidal materials. Instead of fully conjugated polymers we focus on non-conjugated polymers doped with dyes that can act as FRET donors and acceptors. The ambitious end goal of this project is to design a colloidal particle which can self-report the forces acting upon it in the form of FRET efficiencies. We want to measure these forces using confocal microscopy which can give us a quantitative interparticle force map in three dimensions with high temporal resolution. We would have an ideal system to explore the distribution of forces in colloidal systems, ranging

Figure 8.2 – Overview of the system and its proposed operation as described in the introduction.

from highly attractive systems such as colloidal gels, to heterogeneous force networks in colloidal glasses.

In this chapter we make the first steps towards self-reporting colloidal FRET force sensors. The process starts with chemistry: we need to grow polymers on the surface of SiO_2 colloids and dope these polymers with FRET donor and acceptor molecules. We have tried growing a number of different polymers, but in the end poly(methyl methacrylate) gave the best results. When it came to doping we had to choose between coupling the dyes after the polymerisation or starting with the synthesis of labelled macromonomers. We grow poly(methyl methacrylate) (PMMA) polymers on the surface of SiO_2 colloids via a surface initiated reversible addition–fragmentation chain-transfer (si-RAFT) polymerisation [19, 20]. We grow these surface grafted polymers from RAFT agent coupled to the colloids surface via silanization. The polymers are doped with a small molar fraction of functional monomer to which we can couple fluorophores, either BODIPY-FL or BODIPY-TMR, a FRET donor and acceptor respectively (Fig. 8.2 top).

As two sensor colloids come closer together there is a point at which the surface grafted polymer brushes start to interact. This interaction can

come in various forms: the polymer brushes can either compress or interdigitate. Both give a force-distance relation that is non-zero and it is these forces we want to measure. The interdigitation or compression of polymer brushes will locally, where the two colloids interact, increase the concentration of FRET donors and acceptors. As FRET efficiency scales with the distance between donor and acceptor, $E_F \propto \frac{1}{1+r_{da}^6}$, the increase in concentration will lead to a local rise in FRET efficiency at the interface (Fig. 8.2 bottom).

We choose to dope all polymers with the FRET donor and acceptor instead of doping some particles with the donor and some with the acceptor. While the latter option may make sense, since it ensures the baseline FRET efficiency is zero when there is no contact, it does have a drawback. In the separately doped scenario we can only measure when by chance two differently dyed particles interact. When we dope both particles with both dyes we can measure independently of contact geometry.

After synthesising the polymer brushes on the colloidal particles we aim for proof-of-principle spectroscopic and microscopic measurements. In addition, we perform Brownian dynamics simulations on a model based on polymers in good solvents, allowing us to explore the parameter space of our system and tune our future experiments and approaches.

Materials & Methods

Synthesis of FRET force sensor

All chemicals are purchased from Sigma-Aldrich unless indicated otherwise.

The force sensor design is based on a grafting from approach to grow polymers from the surface of a colloidal sphere to create a hairy surface. We grow poly(methyl methacrylate) using Reversible Addition–Fragmentation chain-Transfer (RAFT) [21] polymerisation with 0.01% of monomers replaced by either a fluorescent macromonomer or with a monomer with a functional group capable of coupling to a fluorescent dye after the polymer synthesis. The macromonomer approach was not successful. We used N,N-diisopropylethylamine (DIPEA) as a catalyst during the coupling step of dye to monomer. This catalyst interfered with the RAFT polymerisation reaction, resulting in very short polymers and an incomplete reaction. The post-polymerisation dye coupling did work as the functional monomer seemed to be compatible with

our RAFT synthesis. Apart from PMMA we also tried the polymerisation with polystyrene and poly(*tert*-butyl acrylate); both were unable to polymerise successfully with our chosen RAFT agent.

Functionalisation of the colloidal surface

To grow polymers from the surface of colloids we modify the surface of SiO₂ colloids with a diameter of 4.28 μm (bought from Microparticles, GmbH) with Cyanomethyl [3-(trimethoxysilyl)propyl] trithiocarbonate, a RAFT agent with a trimethoxysilyl group capable of coupling to the silanol group on the surface of the silica colloid. We suspend 0.5 g of silica colloids in 30 mL acetonitrile and add 0.1 μL (0.4 μmole) of the RAFT agent; this amount of RAFT agent should result in a theoretical molecular surface density of 0.65 nm⁻². After 16 hours at 70 °C under vigorous stirring we clean the silica particles by centrifugation and resuspension steps in fresh acetonitrile. Finally we dry the modified particles in a vacuum oven.

Surface-initiated RAFT polymerization

We perform the RAFT polymerisation in 8 mL of solvent per reaction, of which 4 mL is liquid methyl methacrylate monomer. We would like to ensure that, given the 4 mL (37.5 mmole) of monomer, the amount of free RAFT agent plus the amount of bound RAFT agent will give polymers with the target degree of polymerisation, 1250. We keep these volumes constant by changing the amount of free RAFT agent in solution, Cyanomethyl dodecyl trithiocarbonate. The free RAFT agent is a close analogue to the silane RAFT agent with a close chemical makeup. Using this approach we end up with the same polymer free in solution as we have grafted on the silica colloids. We use the free polymer to do spectroscopic analysis.

The synthesis proceeds as follows: we suspend $1 \cdot 10^{-7}$ mole equivalent of RAFT agents attached on silica spheres and $3 \cdot 10^{-5}$ mole free RAFT agent (Cyanomethyl dodecyl trithiocarbonate) in a mixture of 4 mL 1,4-dioxane and 4 mL methyl methacrylate (MMA). Based on the total amount of RAFT agent in the reaction and the target degree of polymerisation we add $3.8 \cdot 10^{-6}$ mole of 2-Aminoethyl methacrylate hydrochloride to reach a doping degree of 0.01%. This functional monomer is used in a later stage to couple the fluorescent dyes, which will form the FRET pair, to the polymer. The reaction is initialised by $6 \cdot 10^{-6}$ mole 2,2'-Azobis(2-methylpropionitrile) (AIBN). We put the reaction mixture in a 25 mL glass vial with an airtight cap. To get rid of the oxygen we bubble the reaction mixture with dry N₂ for 30 minutes followed by 5 vacuum and N₂ refilling cycles. We let the reaction stir for 24 hours at 70 °C after

which we are left with a solid block of polymer at the bottom of the vial indicating a high degree of conversion.

The addition of the functional monomer 2-Aminoethyl methacrylate hydrochloride gives us a means of coupling dyes to the polymers after the RAFT synthesis. We use the FRET pair BODIPY-FL and BODIPY-TMR, both purchased from Lumiprobe (Fig. 8.5). These dyes have a N-hydroxysuccinimide (NHS) ester functional group and easily couple to the amino-group on the incorporated monomer (Fig. 8.3) [22]. We add both fluorophores to the dissolved polymer at the desired concentration and put the mixture on a rotary wheel for six hours to ensure homogeneous distribution of fluorophores. We start the coupling process by the addition of 100 μL N,N-diisopropylethylamine (DIPEA), which acts as a catalyst. After 16 hours of continuous stirring at room temperature we continue with the cleanup.

To clean the reaction products and separate bulk polymer from grafted polymer we start by adding ~ 10 mL of 1,4-dioxane to the reaction product and fully dissolve the polymer over a period of two days on a rotating wheel. We separate free polymer from grafted polymer by centrifugation and further clean the grafted particles with centrifugation and resuspension cycles in 1,4-dioxane. We suspend the particles in a refractive-index matched mixture of toluene and acetone. The free polymer is further purified by precipitation from 1,4-dioxane into ice-cold hexane. After drying the recovered polymer in a vacuum oven, we repeat the precipitation one more time and dissolve the product in a small volume of the same solvent mixture of toluene and acetone.

Sample preparation and measurement

For optimal confocal microscopy imaging we need to minimise the scattering of light at the emission wavelengths. The solvent mixture used in this study, toluene and acetone, is designed in such a way that it matches the refractive index of the silica particles and minimises scattering. We determine the optimal ratio via UV-VIS spectroscopy of solvent samples with different volume ratios of toluene to acetone, $\rho_{\text{toluene}} = \frac{V_{\text{toluene}}}{V_{\text{total}}}$, with a constant concentration of silica particles, 3 mg mL⁻¹. This should have a minimum in the absorption at the ratio which gives the best match in refractive index (Fig. 8.4). We gain this information over a range of wavelengths from 500 to 600 nm, and choose to use 575 nm to determine the ratio as this is the emission wavelength of the FRET acceptor, BODIPY-TMR. We fit the measured absorption values with a generic second-order polynomial and determine its minimum. This gives us an optimal ratio of $\rho_{\text{toluene}} = 0.67$. We use this mixture in all our sample preparations and measurements both of the colloidal particles, free polymer,

Figure 8.3 – (top) Structure of BODIPY-FL. (bottom) Structure of BODIPY-TMR.

Figure 8.4 – Absorption at 575 nm of silica particles suspended in mixtures of toluene and acetone. The solid red line is a fit to a second-order polynomial function. We find the absorption minima at $\rho_{\text{toluene}} = 0.67$ as indicated by the vertical dashed line.

and free dyes.

All fluorescence emission measurements for the free polymer are performed on a Cary Eclipse fluorescence spectrometer and the UV-VIS absorption spectra are measured on a Shimadzu UV-2600. For the FRET microscopy measurements of the colloids, we use a Zeiss Laser Confocal Scanning Microscope (CLSM) LSM5, with excitation laser lines at 488 nm (Argon laser) and 543 nm (Helium–Neon laser) and two emission detection bands, one between 505–530 nm and the second for wavelengths from 560 nm and longer. Detection of emission intensities in both channels occurs on a per-pixel basis with a photon-multiplier tube (PMT) coupled to a 16-bit ADC, which we give identical settings for both channels, as to not bias the intensity of either channel. We capture two dimensional images of $512 \text{ px} \times 512 \text{ px}$ or $123 \mu\text{m} \times 123 \mu\text{m}$. By alternating excitation with 488 nm (donor excitation) or 543 nm (acceptor excitation) and measuring in both detection channels we get data for I_{DD} , I_{DA} , I_{AA} , and I_{AD} . This gives us enough information to calculate a relative FRET efficiency on a pixel-by-pixel basis via:

$$F^* = \frac{I_{DA}}{(I_{DD} + I_{DA})} \quad (8.1)$$

in which we only take pixels into account with an intensity in both channels above a certain threshold, to avoid spuriously high or low FRET-ratios due to noise and floating-point errors when dividing very small numbers [23].

Simulations

All simulations use a Brownian dynamics integrator as implemented by the simulation package HOOMD-Blue (v2.2.1) [24, 25, 26] running on two NVIDIA GTX 1080 Ti GPUs in single-precision mode. We use

the classical Kremer–Grest bead-spring model for a polymer in a good solvent [27]. In this model beads connected with Finite Extensible Non-linear Elastic (FENE) potentials and interacting via the purely repulsive Weeks–Chandler–Anderson (WCA) potential (Equations 1.1 & 8.3), represent the polymers under study.

$$U_{FENE}(r) = -\frac{1}{2}\epsilon R_0^2 \log\left(1 - \frac{r - \Delta}{R_0}\right) \quad (8.2)$$

$$U_{WCA}(r) = \begin{cases} 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right] + \epsilon, & \text{if } r < 2^{1/6}\sigma \\ 0, & \text{otherwise} \end{cases} \quad (8.3)$$

We use $\epsilon=1$, $\sigma=1$, $R_0=1.5 \cdot R_{\text{bead}}$, $\epsilon=30$ [28], and $\Delta=(d_i + d_j)/2 - 1$ with d_i and d_j the diameters of particle i and j respectively. In our simulations we have two walls onto which we anchor 400 bead chains (N_p), each consisting of 128 beads (N_b), forming two grafted surfaces in opposite direction (Fig. 8.10). All beads have the same WCA potential interaction with the walls as they have with each other. The polymers on the two opposite surfaces extend towards each other along the z-axis; the simulation box is therefore only periodic along the x-axis and y-axis. We change the box size in x and y and the spacing between chains to change the overall grafting density, so that all our simulations are done with a constant number of beads, $N=103200$. The simulations are run with a step size of $5 \cdot 10^{-5} \tau_b$, where τ_b is the Brownian self-diffusion time of the beads. After equilibrating for $1 \cdot 10^8$ steps we decrease the separation between the two surfaces by $0.2 \cdot R_{\text{bead}}$ every τ_b , to simulate two surfaces approaching. We take a snapshot of the system every 100,000 timesteps which we use for further analysis.

Calculation of the FRET efficiency from simulations

For a system with a single donor and a single acceptor moiety the energy transfer efficiency is described by the Förster equation:

$$E = \frac{1}{1 + \left(\frac{r_{da}}{R_F}\right)^6} \quad (8.4)$$

where r_{da} is the distance between donor and acceptor and R_F is the Förster radius; the distance between donor and acceptor at which the efficiency of energy transfer is 0.5. Instead of describing the efficiency in terms of distance and Förster radius, we can describe it as the ratio between the rates of energy transfer from donor to acceptor, k_F , and that

of direct photon emission from the donor, k_D :

$$E = \frac{k_F}{k_F + k_D} = \frac{1}{1 + \left(\frac{k_D}{k_F}\right)} \quad (8.5)$$

In the case of a multitude of fluorophores present the total rate of energy transfer, k_F , will be a sum of the transfer rates to all acceptors, $k_F = \sum_i^{N_a} k_{F,i}$, where N_a is the number of acceptors in the system. With the information that $\left(\frac{k_D}{k_F}\right) = \left(\frac{r_{da}}{R_F}\right)^6$ (Equation. 8.4 & 8.5) we can write the FRET efficiency in our system as the mean of the energy transfer from every donor to every other acceptor:

$$E_F = \frac{1}{N_d} \sum_i^{N_d} \frac{\sum_j^{N_a} \left(\frac{R_F}{r_{ij}}\right)^6}{1 + \sum_j^{N_a} \left(\frac{R_F}{r_{ij}}\right)^6} \quad (8.6)$$

In the case of simulations with a variable acceptor to donor ratio we keep the concentration of donor beads constant and only vary the amount of acceptor beads. We start the calculation of the FRET efficiency by selecting 100 different random distributions of donor and acceptor beads. All calculations of FRET efficiencies in our simulations are averaged over these 100 configurations and we use the same 100 selections for every distance between the two walls. We set $R_F = 3.0 \sigma$ for all our calculations and set the donor doping degree to 0.01 times the total number of beads in the system unless indicated otherwise.

We can do these calculations of FRET efficiency via equation 8.6 in our simulations because we have all the necessary information; we know the distances between every donor-acceptor pair in the system. For our experimental measurements we do not have this information. We measure the ensemble FRET efficiency — averaged over all the possible donor-acceptor possibilities.

As our polymers are randomly labelled, the distribution of donors and acceptors at the interface between two grafted colloids can be approximated as homogeneous in space. In this case the probability to find an acceptor at a distance r from a donor is:

$$P(r) = 4\pi N_{av} [A] r^2 dr \quad (8.7)$$

where $[A]$ is the molar concentration of acceptors in moles m^{-3} and N_{av} is Avogadro's number. From this equation we can calculate the number of acceptor molecules, N_A , we expect to find in shell of thickness δr by integrating over the shell thickness. The N_A acceptors in the shell of thickness δr contribute $N_A k_A$ to the sum of the overall FRET efficiency.

In the continuum limit of infinitesimally small δr the Förster relation becomes:

$$E_F = \frac{4\pi N_{av}[A]R_F^6 \int_{r_0}^{\infty} r^{-4} dr}{1 + 4\pi N_{av}[A]R_F^6 \int_{r_0}^{\infty} r^{-4} dr} \quad (8.8)$$

where the integral runs from a minimum distance, r_0 , towards infinity. This minimum distance of r_0 is necessary to exclude unphysical states where molecules would overlap in forbidden ways. The integral is analytically solved as $4\pi N_{av}[A]R_F^6 \int_{r_0}^{\infty} r^{-4} dr = \frac{4}{3}\pi N_{av}[A]R_F^6 r_0^{-3}$. With this result we arrive at our final prediction for the FRET efficiency in a system with a homogeneously random distribution of fluorophores:

$$E_F = \frac{\frac{4}{3}\pi N_{av}[A]R_F^6 r_0^{-3}}{1 + \frac{4}{3}\pi N_{av}[A]R_F^6 r_0^{-3}} \quad (8.9)$$

The qualitative behaviour of this equation can be captured by substituting $C = \frac{4}{3}\pi N_{av}R_F^6 r_0^{-3}$:

$$E_F = \frac{C \cdot [A]}{1 + C \cdot [A]}. \quad (8.10)$$

By way of this substitution all constants are combined in a single fitting parameter which captures all of the experimental specifics of the system under study. The resulting simplified expression captures the general shape of the predicted FRET efficiency as a function of acceptor concentration in the case of homogeneously and randomly distributed donor and acceptor molecules throughout the system of interest.

Results and Discussion

If our idea for the colloidal force sensor is feasible we should observe an increase in FRET efficiency when doped polymer chains on one particle start to interact with polymers on another particle, effectively either interdigitating or compressing the polymers on either surface. To test this central ansatz we take the free polymer from the synthetic procedure and measure its emission spectrum at donor excitation, 488 nm, for a large range of concentrations, C_p . The highest concentration we could reach with the available material was, $C_{p,0} = 85 \text{ mg mL}^{-1}$. We dilute the sample by a factor 2 after each measurement. With this method we measure concentrations in the following series: $C_p = 85, 43, 21, 11, 5.3, 2.6, 1.3, 0.66, 0.33$, and 0.17 mg mL^{-1} (Fig. 8.7A).

Figure 8.5 – Absorption and emission spectra for the NHS BODIPY dyes, measured for BODIPY-FL (emission: green closed circles, absorption: green open circles) and BODIPY-TMR (emission: red closed triangles, absorption: red open triangles). The shaded region is the overlap region between the emission of the donor and absorption of the acceptor. The excitation lines used on our confocal are indicated with two dashed lines at 488 nm and 543 nm.

We calculate the relative FRET efficiency, or ratiometric FRET efficiency, for the free polymers in solution as $F^* = I_{DA}/(I_{DA} + I_{DD})$, where I_{DD} are I_{DA} are the emission maximums for the donor and acceptor respectively both for excitation at the donor excitation wavelength of 488 nm. This method does not calculate a real FRET efficiency; we do not correct for leakage of donor emission in the acceptor channel and vice versa. Since we are only interested in relative changes in FRET efficiency as we increase the polymer concentration, we presume that this should suffice.

Our initial approach tried to decompose the emission spectra of the polymer with attached donor and acceptor fluorophores into the respective separate spectra from donor or acceptor; the polymer emission spectrum, $S(\lambda)$ is a linear combination of the two components as $S(\lambda)_{\text{total}} = x_1 S(\lambda)_{\text{donor}} + x_2 S(\lambda)_{\text{acceptor}}$. Unfortunately, there appears to be a significant shift in emission peak positions with respect to polymer concentration. From a 3 nm shift at low concentrations to a 14 nm shift at higher concentrations (Fig. 8.6). We think this shift is caused by stacking of dye molecules at high polymer concentrations. We therefore allow the base spectra to have a shift towards longer wavelengths. Minimising the difference between the measured full spectrum and the one constructed via a linear combination, gives us x_1 , and x_2 . With the two factors we can reconstruct the spectrum and calculate the relative FRET efficiency F^* as the ratio between the area of the acceptor emission versus the total area, $F^* = \frac{I_A}{I_D + I_A}$ (Fig. 8.7B).

The measured FRET efficiencies show the expected dependence on polymer concentration and FRET pair ratio; as the polymer concentration increases every sample shows an increase in FRET efficiency

Figure 8.6 – (A) Acceptor emission peak as a function of polymer concentration. The emission peak from a non-coupled BODIPY-TMR is shown in black. (B) Peak position as a function of polymer concentration.

Figure 8.7 – (A) Emission spectra of polymers doped at a ratio, $a = 1$ at polymer concentrations, from top to bottom: $C_p = 85, 43, 21, 11, 5.3, 2.6, 1.3, 0.66, 0.33$, and 0.17 mg mL^{-1} . The spectra are normalised with respect to the maximum of the emission peak of the donor. (B) The relative FRET efficiency calculated from the emission spectra after spectral decomposition, for acceptor to donor molar ratio, from top to bottom, $a = 1.0, 0.8, 0.6, 0.4, 0.2, 0.1, 0.05$ & 0.01 . (C) Same data as B normalised with respect to the relative FRET efficiency at $C_p = 0.17 \text{ mg mL}^{-1}$.

(Fig. 8.7A & B). As polymer coils come close together their coil size decreases as an effect of crowding. As their size decreases, locally the concentration of both FRET acceptors and donors increases, with an overall increase in FRET efficiency as a result. The ratio of acceptor to donor molecules, a , also has a clear effect; with an increase in acceptor concentration the FRET efficiency at high dilution, F_0^* , increases, from 0.12 at $a = 0.01$, to 0.6 at $a = 1.0$. Effectively, these free polymers already form a crowding sensor with possible applications in biological systems such as the interior of cells where crowding effects are thought to regulate transport [29, 30], facilitate dynamical compartmentalisation [31, 32, 33], and control protein folding [34].

For our sensor we need a baseline of almost no energy transfer (ET), so F_0^* should be as low as possible. With a low baseline we have the most optimal signal-to-noise ratio and the best chance to detect the smallest increases in FRET ratio. When the polymer concentration increases the effect on the FRET efficiency should be as large as possible. We are therefore looking for a sample with a small F_0^* and a large increase in the relative FRET efficiency, F^*/F_0^* . To this end we also plot the increase in FRET efficiency normalised to its zero value (Fig. 8.7C). The dependence here on a is not as straightforward as might have been expected. As a general observation, higher ratios of acceptor to donor concentration do not lead to a stronger increase in F^* . In fact the opposite effect seems to be at play; samples with a lower ratio a appear to have the strongest increase in energy transfer efficiency compared to the baseline.

Our experiments on free doped polymer have shown the expected behaviour. With an increase of polymer concentration we observe an in-

Figure 8.8 – Confocal images for the acceptor emission (**A**), donor emission (**B**), and calculated relative FRET efficiency (**C**). All images are made with an excitation laser at 488 nm and at $\alpha = 0.6$. Pixels with intensities lower than the cutoff value, I_c , are set to zero.

crease in relative FRET efficiency. Polymer coils in a more concentrated solution will decrease their radius of gyration slightly due to crowding until at a critical concentration c^* coils start to interpenetrate. Both effect combined result in a local increase in the concentration of donor and acceptor pairs. The result is the observed increase in FRET. The next step is to test the sensor-particles with the polymer grafted on their surface. We take dilute sensor-particle suspensions and add 100 mg mL^{-1} of linear polystyrene, $M_n = 99,000 \text{ Da}$ and $M_w = 105,500 \text{ g mol}^{-1}$, as a depletant. This large polymer chain introduces an attractive force between particles called the depletion force. This attraction is due to entropic reasons; colloidal particles have an excluded volume with the polystyrene coils based on the radius of the polymer coil. The polymer globules can not explore this space, it is therefore favourable to minimise the total excluded volume in the system. The minimisation is achieved by clustering colloids together such that the excluded volume regions overlap and more space is available for the polymers to explore. The aggregation of colloids thus increases the entropy of the system since the polymer globules have more volume to explore.

The depletion attraction between the particles ensures strong contact between particles and gives us the most optimal testing bed for our sensor-particles. The particles form gel-like sparse colloidal aggregates under the influence of the attractive forces. We image the clusters using laser scanning confocal microscopy (Fig. 8.8A & B).

We calculate the relative FRET efficiency, F^* , on a pixel-by-pixel basis according to $F^* = I_{DA}/(I_{DD} + I_{DA})$. To remove the spurious and noisy pixels in the background and inside the particles we only perform the calculation on pixels which have intensities both in the acceptor and donor channel above a certain cutoff intensity, $I_c = 1 \cdot 10^4$ [23]. The resulting images of the relative FRET efficiency show a clear signal from the

Figure 8.9 – (A) Probability distribution of the relative FRET efficiency F^* calculated over all pixels in the image. Calculated for different n_A/n_D . Solid lines are Gaussian fits as described in the text. The plots are offset for clarity. (B) Relative FRET efficiency minus the efficiency at $a = 0.01$. The dashed line is a fit to equation 8.11.

particle surfaces (Fig. 8.8C).

We start our analysis by looking at the global distribution of relative FRET efficiencies across all pixels in the image. We calculate the distribution $P(F^*)$ and fit a Gaussian curve of the form $P(F^*) = \frac{A}{\sqrt{8\pi\sigma^2}} \exp -\frac{(F^*-\mu)^2}{2\sigma^2}$ to each distribution (Fig. 8.9A). From the fit we obtain the mean value (μ) and the standard deviation (σ), which we plot as a function of acceptor to donor molar ratio, a . The global FRET efficiency follows the expected trend: as a increases and there are more acceptors for every excited donor, so does the average FRET efficiency (Fig. 8.9B). The FRET efficiency is clearly limited by the number of acceptors, as increasing it also increases the FRET ratio. We fit the data with the FRET efficiency prediction for a system of multiple acceptors and donors with a random yet homogeneous distribution (Equation 8.10). In these experiments we do not measure the absolute FRET efficiency E_F , but a relative FRET ratio, F^* . The FRET ratio we measure has a baseline higher than zero; therefore, we do not plot F^* , but $F^* - F_{0.01}^*$, the relative FRET efficiency minus the efficiency found at the lowest concentration in our measurements:

$$F^* - F_{0.01}^* = \frac{C \cdot a}{1 + C \cdot a} \quad (8.11)$$

In general our system conforms to our expectations in relation to a change in the molar ratio between FRET moieties. However, the power of our proposed colloidal force sensor lies with the ability to visualise an increase in relative FRET efficiency at the interfaces between colloids where forces are being exerted on both particles across the interface. Unfortunately we were unable to find an increase in FRET at the interfaces between the sensor colloids compared to the rest of the surface of the colloids (Fig. 8.8C). At every acceptor-donor ratio tested we found a homogeneous distribution of FRET efficiencies across the surfaces of the colloidal particles.

There are several possibilities which could cause this setback. There is a category of experimental corrections which would give a fairer FRET ratio. So far we have only used a very simple way to calculate a relative FRET ratio. This method does not take into account leakage of donor emission in the acceptor channel or acceptor emission due to direct excitation by the donor excitation wavelength. From the spectra of the dyes we can see that indeed the 488 nm laser will directly excite the acceptor dye and that there will be some, albeit it limited, emission of the donor in the acceptor band. Apart from band-leakage there is the issue of the relative quantum efficiencies of BODIPY-FL (donor) and BODIPY-TMR (acceptor). According to the manufacturer their fluorescence quantum yields are 0.95 and 0.97, respectively. These values are high and very close and we do not expect them to have a significant impact on our measurements. More importantly, we assume that the spectral response of our photo-multiplier tube (PMT) detectors is flat. It is highly unlikely that the PMTs have the same response level around 510 and 560 nm. However, due to the proprietary nature of the equipment we are unable to get information about the exact shape of the spectral response curves of the PMTs in our confocal setup. Correction factors for all the errors mentioned above have been derived, but all these errors operate on a global scale, that is, the correction is the same for every pixel. We should therefore still be able to discern a relative difference in FRET should our sensors function correctly. It is likely that design choices in the system itself are the cause of our inability to observe the expected increase in FRET at particle contact.

Our experimental design, doped polymers grafted to the surface of colloids, has a large amount of changeable parameters. All parameters add up to a very large phase space which is difficult to explore experimentally. The most obvious experimental parameters are the grafting density, molar ratio between acceptors and donors, the distribution of FRET moieties on the polymer chains, and the length of the polymers. We expect the grafting density of polymers to be of the highest importance. Due to the high amount of added silane-RAFT agent during the synthesis of our sensor-particles, the grafting density of polymers on the particle surface is close to its experimentally viable maximum. The result is that the polymers on the surface are already in a highly stretched state and compression or interdigitation of the chains requires a high pressure, with associated energies $\gg k_B T$. This is an energy scale we possibly cannot reach with forces induced by thermal fluctuation of particles, gravity, or depletant-based attractive forces. To scan the available parameter space in a shorter timescale we decided to perform Brownian Dynamics simulations on the well known Kremer–Grest model and focus on the influence of the grafting density.

Our simulations consist of two grafted flat walls which we bring closer together in small decrements, Δd , after the system has equilibrated for

$500 \tau_B$. We choose $\Delta d = 0.2 \sigma$ with a relaxation time of $1 \tau_B$ in between each compression step; these parameter choices avoid numerical errors due to extreme particle overlap. Each wall has 400 chains each consisting of 128 beads grafted on its surface in a square lattice configuration. The two grafted surfaces are facing each other along the z-axis of the simulation box (Fig. 8.10). The simulation box is only periodic in x and y and we change the sizes along these axes to tune the grafting density.

In order to gain information about the range of grafting densities we should probe we need to know the average radius of gyration, R_g , for one of our chains confined to a wall. To this end we start by simulating a single chain attached to a wall for $5000 \tau_B$ and calculate R_g , as follows:

$$R_g^2 \equiv \frac{1}{N_b} \sum_i^{N_b} (\mathbf{r}_i - \langle \mathbf{r} \rangle)^2 \quad (8.12)$$

where $\langle \mathbf{r} \rangle$ is the average position of all beads in a chain and the sum runs over all beads in a single chain.

We average the calculated R_g over the last 100 simulation snapshot each separated by $5 \tau_B$. Using this method we find $R_g = 7.1 \sigma$. A theoretical prediction for a chain of 128 beads would be $R_g \sim \sqrt{\frac{1}{6} * N_b * \sigma^2} = 4.6 \sigma$. The two values are close, however the prediction only works for a chain in a theta solvent. In our case the polymer is dissolved in a good solvent and furthermore is hindered by the presence of a wall, or the particle surface in the experiments. As a result our polymer chains have a higher average radius of gyration.

From the calculated value for R_g we can determine the grafting density where anchored chains just begin to interact, the weak brush regime. This grafting density follows as: $\rho_g = 1/R_g^2 = 0.02 \sigma^{-2}$. Since the goal of our simulations is to determine the influence of grafting density on our measured FRET efficiency we simulate a series of grafting densities around $0.02 \sigma^{-2}$: $\rho_g = 0.004, 0.008, 0.014, 0.02, 0.08, 0.14$, and 0.2 . Our ideas are based around the assumption that two doped polymer brushes which get pushed together with some force will result in a locally higher concentration of dyes due to compression of the polymer coils or interdigitation of the chains. By simulating in a region of grafting densities varying from below $0.02 \sigma^{-2}$, a system dominated by surface anchored coils, to above this critical value — a surface covered with compressed and stretched coils — we hope to explore and identify the design that maximises the sensor sensitivity.

Grafting density has a large effect on the behaviour of our sensor in simulations. As we increase the grafting density and move from a mushroom regime into a brush regime we find much lower relative increases in FRET efficiencies as a function of the total bead concentration in our sim-

Figure 8.10 – Computer renderings of the simulations studied in this chapter. We show a small slice, 20σ in thickness centred around zero, in y with the full extend of the simulation box in the x and z direction. The four snapshots are taken at (top to bottom) $C_b = 0.049, 0.067, 0.11$, and 0.26 . The green spheres represent the anchor point of the polymers to the walls.

Figure 8.11 – (A) Relative FRET efficiency, $E_F/E_{F,0}$ as a function of the concentration of beads in our simulation box, C_b . Calculated for (left to right) grafting ratio: $\rho_g = 0.004, 0.008, 0.014, 0.02, 0.08, 0.14$, & 0.2 . (B) Same data as in (A) plotted as a function of the pressure on the moving surfaces, P_{wall} . (inset) Onset pressure, P_0 , as a function of grafting density, ρ_g . The solid line is a power-law, $P_0 = A \cdot \rho_g^b$, with a exponent, b , equal to 1.0 . The dashed line indicates the point $\rho_g = 0.02$.

ulation box (Fig. 8.11 A). We choose to plot our simulation data against the bead concentration as this is the most comparable parameter to the polymer concentration we used in our spectroscopic measurements. For the simulations with grafting densities below $\rho_g = 0.02 \sigma^{-2}$ we find an increase in FRET efficiencies starting at low bead concentrations while higher grafting densities lead to much later onsets of FRET efficiency increase which also doesn't increase as much as the lower grafting densities do. Unfortunately, the dependence of FRET on the grafting density is not as simple as that; there appears to be an optimum in grafting density which gives high relative FRET efficiency increases while retaining a low onset concentration of beads. We find this optimal behaviour at the intermediate grafting densities of $\rho_g = 0.014$ & 0.02 .

With our experimental system we hope to measure and visualise interparticle forces. However, we do not have access to local polymer concentrations. To make comparison with experiments more appropriate we re-plot the calculated FRET efficiencies as a function of pressure exerted on the moving walls of the simulation box. We find the same behaviour as when plotted against the bead concentration although this new plot makes it easier to compare our results to our intended design parameters for the experimental system. Our main hypothesis for why we did not observe anything in experiments are the large forces necessary to observe a FRET increase when the grafting densities on the particles are high. With our simulations we can confirm this to be plausible. As we increase the grafting density we observe a corresponding increase in the onset pressure, P_0 — the pressure where we begin to observe an increase in FRET efficiency. In fact, the relation between the grafting density and onset pressure is linear over three orders-of-magnitude in grafting density (Fig. 8.11B & inset).

In our experiments we investigated the effect of the doping ratio a on

Figure 8.12 — **(A)** Relative FRET efficiency, $E_F/E_{F,0}$ as a function of the concentration of beads in our simulation box, C_b . Calculated for (top to bottom) acceptor-to-donor ratio: $a = 1.0, 0.8, 0.6, 0.4, 0.2, 0.1, 0.05, \& 0.01$. **(B)** Same data as in **(A)** plotted as a function of the pressure on the moving surfaces, P_{wall} . The solid lines indicate the error ranges.

the measured relative FRET efficiency. With our simulation model we can investigate the effects in more detail; our simulations give us direct information on the relation between FRET efficiency and the distance between two grafted surfaces. This relation does not follow directly from our experiments. We therefore simulate the system at a given grafting density of $\rho_g = 0.014$ and calculate the FRET efficiencies for a series of acceptor to donor ratio — $a = 1.0, 0.8, 0.6, 0.4, 0.2, 0.1, 0.05$, and 0.01 — as a function of bead concentration between the two surfaces.

With increasing the acceptor to donor ratio the baseline FRET efficiencies increase to higher values. We find a similar relationship between the ratio and the FRET efficiency at high concentrations (Fig. 8.12A). The effect of the ratio on the response of the system is best studied by considering the relative increase in FRET efficiency, $E_F/E_{F,0}$ (Fig. 8.12B). We find qualitatively similar behaviour for every ratio tested. From low to intermediary bead concentrations the FRET efficiency shows a linear response to the bead concentration for all ratios under investigation. At higher bead concentrations the responses start to diverge from each other. Low ratios have a stronger increase in FRET efficiency. However, for these Low ratios the absolute values are very small and thus hard to experimentally measure. The total increase in FRET efficiency all lie between $4.5 \times$ to $6 \times$, sufficient for our purpose.

Our simulations have confirmed our suspicion that changing the acceptor to donor ratio does not change the fundamental behaviour of our envisioned force probing colloids. The only major effect seems to be an overall increase in FRET efficiencies resulting in potentially more signal we can measure in experiments. A more useful tuning parameter is the grafting density of polymers on the surfaces of the colloids. It is clear from our simulations that the grafting density controls the pressure response range of the reporter colloids and it is therefore crucial to correctly tune in future experiments.

Conclusion & Outlook

A major step forward for the world of Soft Matter would be the development of a method to quantitatively measure and visualise the forces in a colloidal soft matter system at the same time. In this chapter we have made the first steps towards such a method for colloids. We designed a self-reporting colloidal particle, which can report on the forces it experiences from its neighbouring particles in a packing.

To this end, we grafted polymer brushes on the surface of silica colloids that were sparsely doped with FRET acceptor and donor molecules. The idea was that whenever two particles come close enough together to exert forces onto one another we could measure these by measuring the FRET efficiency in the two compressed surface grafted brushes using confocal microscopy. The general idea is that compression or interpenetration of the brushes locally enriches the concentration of FRET moieties and thereby increases the local FRET efficiency.

We were successful in grafting polymers on the surface of our silica colloids and doping these with FRET donor and acceptor fluorophores, BODIPY-FL and BODIPY-TMR respectively. These polymers behaved as expected; their FRET efficiency increased at higher concentrations. Unfortunately we were unable to observe a significant increase in FRET efficiency at the contact between particles. As the colloids were surface-modified with an excess of RAFT agent, the final grafting density of polymers is at the higher end of what is experimentally viable. In simulations we found a linear relationship between grafting density and the pressure needed to start seeing an increase in FRET efficiency. This picture matches with the experimental findings — at high grafting densities there needs to be an excessively large pressure to compress the brushes, which we cannot easily reach in experiments. To have any chance of observing a change in the FRET ratio the pressure exerted in the particles via depletion should at least match the pressure of the grafted polymer brush on the surface of the particles; in other words the number densities should be similar. If we assume that polymer grafting density is such that all polymers are separated by a distance equal to their radius of gyration then: $\sigma = R_g^{-2}$ and the grafting density becomes: $\rho \approx R_g^{-3} = \rho^*$. In this case the number density is equal to the overlap number density. For our depletent we use linear polystyrene with a molar mass of 105,500 g mole⁻¹. The radius of gyration of this polymer is approximately 9 nm [35]. This gives us an overlap number density of $\rho = R_g^{-3} = 1.4 \cdot 10^{-3} \text{ nm}^{-1}$. At a concentration of 100 mg mL⁻¹ we have a number density of $6 \cdot 10^{-4} \text{ nm}^{-1}$, well below the overlap number density. Furthermore, any slight increase in the grafting density of polymers on the surface of the particles will

Figure 8.13 – Calculated FRET efficiency as a function of bead concentration between the two walls calculated for the conjugated polymer model. We calculate the efficiency at acceptor doping degrees (bottom to top) $a_{\text{acc}} = 0.001, 0.002, 0.003, 0.004$, and 0.005 . (**inset**) Same data, normalised to the FRET efficiency at the lowest acceptor doping degree.

massively increase the pressure as polymers become stretched.

From these simulations it is clear that the focus of future experiments should be on controlling the grafting density. One way to achieve this would be to introduce a competitor, non-RAFT agent of similar molecular weight, silane at the surface modification phase, thereby controlling the final grafting density of sensor polymer.

In this study we used poly(methyl methacrylate) (PMMA) polymers that we doped with FRET fluorophores. In our case these were BODIPY-FL as donor and BODIPY-TMR as acceptor moieties. Our research group has previously measured forces with the use of conjugated polymers, polymers that have a fully conjugated backbone and have therefore useful properties. One of the breakthroughs with this kind of sensor was the measurement of intrapolymer forces of chain extension on a single polymer level [18]. The FRET behaviour of these polymers were successfully described in both simulations and experiments with the same method as we used in this chapter. The key is to treat the entire backbone as a chain of donor molecules with the occasional acceptor dispersed in between. Conjugated polymers show the same behaviour in our simulations as doped PMMA and reach the same increases in FRET efficiency but with fewer acceptors. There is also a lot less variation between each simulation configuration, which would definitely help the reliability of the sensor and its measurements (Fig. 8.13). BODIPY dyes have a very high fluorescence quantum efficiency, but, as most organic dyes, bleach over time under prolonged exposure. Conjugated polymers can combine the best of both worlds: they have high fluorescence quantum efficiencies and are photostable [36]. We therefore think that the future of the colloidal force sensors lies with conjugated polymers.

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GENERAL DISCUSSION

9

Introduction

THIS thesis aimed to investigate the effects of disorder in soft condensed materials on the properties of those materials and how they differ from expectations from conventional rules. In chapter 4 & 5 we focused our attention on colloidal glasses; systems which are dominated by structural disorder. After extensive experimental work we analysed our findings in the context of relaxations in a glass as elastic processes. We extended this analysis by describing the elastic properties of the glass in terms of the load-bearing bonds particles experience with respect to a finite frequency of interest. Our predictions are able to capture the observed global slowdown to a high degree.

In chapter 2 & 3 we added dynamical disorder in the form of weak crystals and structural disorder due to interstitial dopants. We investigated how classical theories of dopant dynamics in such systems break down as a result of the dynamic disorder of the base crystal. We observed markedly slower diffusion of dopants and even clustering and eventual phase separation of dopants.

The first four chapters dealt with spherical isotropic hard-core particles. In the following, chapters 2 & 3, we supplemented structural disorder in the form of glasses with disorder within the constituent particles; we use microgels which are able to (de-)swell as a response to the osmotic pressure of their surroundings. We studied the glass transition of highly asymmetrically sized particle mixtures and binary compressible microgel discs. We found that the experimentally observed fragile-to-strong transition for very soft colloids is not a real transition, but only the result of plotting the relaxation times against the extrapolated volume fraction, ζ , which is not an appropriate state variable.

All previous chapters made us aware that the ability to measure and visualise interparticle forces between colloids would be very valuable. We tried to devise such a method and in chapter 8 we make the first steps towards such a sensor.

In this final chapter we shift our focus and place the results obtained in the previous chapters in a wider scientific context. We finish with a look into the future of soft condensed matter research.

Dynamical Connectivity in Colloidal Glasses

In our study of colloidal glasses we were inspired by the work of Y. Frenkel on the frequency dependence of the behaviour of liquids. Frenkel introduced a microscopic liquid relaxation time, τ , as the average time between relaxation events in a liquid [1]. When the liquid is investigated at times well above this relaxation time, $\tau_0 \gg \tau$, the liquid behaves more as a gas; particles follow ballistic paths until they collide and the system has no elastic resistance to shear. However, at times below τ , $\tau_0 < \tau$, the liquid can be viewed as an elastic medium. This description of Frenkel emphasises the frequency dependence of the behaviour of liquids and was extended upon by Trachenko and colleagues who used the *duality* of liquids to show that thermodynamical properties of liquids are dominated by solid-like vibrations [2]. This dual nature of liquids has more recently been experimentally observed for water [3], confirming it as a valid approach, and a possible route to finally resolve the lacking theory for the liquid state.

Inspired by this frequency-dependent approach to liquids, we tried to describe our experimental data for glasses within a frequency-dependent elastic model where elasticity is determined by the local connectivity of load-bearing bonds between particles. With this approach we successfully connected microscopic features, the local connectivity, Z , to the global dynamical slowdown of the system. We realised that in direct analogy to liquids, the coordination number in our glasses had to be frequency dependent, $Z(\tau_0)$. For a colloidal liquid to support any elastic modes, we need to measure at time scales shorter than the Brownian time scale, $\tau_0 < \tau_B$, hence the frequency of interest for the coordination number in our system lies at the Brownian time, $Z(\tau_0 = \tau_B)$. Our prediction fully described our experimental data without adjustable parameters and is in line with the ideas about fluidity and rigidity emerging as a result of bonds between particles persisting within a certain frequency range.

Even though our system consisted of purely repulsive particles with a Yukawa type pair interaction, there are still effective load-bearing bonds

Figure 9.1 – Colloidal ionic systems made with PMMA particles with different stabilisers. Traditional PHSA base stabilisers give anionic particles, which in our system are the smaller (yellow) particles. Stabilisers based on PDMS give cationic particles (blue, larger). **(A)** Snapshot of the ionic system at a 1:1 number ratio without TBAB **(B)** as in **(A)**, with 0.5 mM TBAB **(C)** as in **(A)**, with 1.1 mM TBAB **(D)** Pair interaction potential, $U(r)$ measured by inversion of $g(r)$. For systems without TBAB (red spheres), 0.5 mM TBAB (green right triangles), and 1.1 mM TBAB (green left triangles). The solid lines are fits to a Yukawa type potential of the form: $U(r) = \varepsilon \frac{\exp(-\kappa r)}{r}$ **(E)** Radial distribution function of the large cationic particles, $g_L(r)$, for the system in panel **A**. **(F)** Probability distribution of angles between pairs of anionic particles on one cationic particle.

in our systems. The finite size of the sample, confined by the sample chamber, ensures this. The potential of mean force, $w(r) = -\ln(g(r))$, does indeed have a minimum at the average particle-particle distance. The addition of a real attractive component to the pair potentials has a major impact on the glass transition behaviour. The influence of attraction has been studied for colloidal glasses with the aid of depletant attraction, whereby the dynamics of the glass phase was studied along the axis of the depth of the attractive potential well, U [4]. The authors found that the glass melts as a direct result of the added attraction, up to a critical attraction strength, $U \approx 3 k_B T$. For higher attraction strength the glass was again a solid. More importantly the authors show that the attractive glass transition is driven by direct particle-particle bonding upon reaching a threshold attraction strength. This behaviour of attractive glasses, where the dynamics are governed by both cages and bonds has also been

observed in rheological studies of these systems as a characteristic two step decay [5].

These findings on attractive glasses opened our interest in the effect of attractions on the glass transition. Especially the limiting case of ionic glasses that consist of two species of opposite charge are interesting, as glasses in these systems can be expected to be dominated by bond formation and not by the cage effects of hard sphere systems [6]. For example, these ionic glasses have been found in atomic zirconium tetrafluoride systems [7]. Ionic colloidal systems have previously been used to study binary crystal formation, but have, to the best of our knowledge, not been used for the specific purpose of studying ionic glasses.

To study these systems we designed a colloidal ionic system consisting of poly(methyl methacrylate) (PMMA) particles with two different stabilisers. Using the poly(12-hydroxystearic acid) (PHSA) based stabiliser leads to negatively charged particles, anions, while the use of polydimethylsiloxane (PDMS) based stabilisers gives cationic particles. The energetically favourable conformation for such a system would be a cubic NaCl type packing, as this maximises the distances between like charged particles. Indeed, experiments on a similar ionic colloidal system found exactly this type of crystal [8]. To avoid the crystal phase we need precise control over the interaction strengths between the different populations. As a proof of concept we use tetrabutylammonium bromide (TBAB) to screen the charges present on both the anionic and cationic particles.

For systems with the same concentration of particles we observe clear effects of TBAB: without any TBAB present the system forms highly open gel-like structures; the cationic particles are surrounded by a limited number of anionic particles, allowing for the appearance of sparse networks (Fig. 9.1A). The distribution of angles between two anionic particles on one cationic particle has two well defined peaks, a sharp peak around 60 degrees and a broad peak centred on 120 degrees (Fig. 9.1F). The structure of the system is the result of a balance between the attractive $\oplus\ominus$ forces and the repulsive $\ominus\ominus$ and $\oplus\oplus$ forces, which all have the same interaction ranges. As we start to add TBAB (0.5 mM) we enter a regime where the sparse network transformed into connected dense blobs of binary packings (Fig. 9.1B). If TBAB does indeed screen the charges this is what we would expect; the addition of TBAB decreases the Debye length, λ_D , and as a result the anionic particles are able to bring the cationic particles closer together. Further addition of TBAB (1.1 mM) complicates matters; at these high levels of TBAB we find binary liquids which appear to have long range repulsion. This would imply that the addition of TBAB inverted the charges on one of the two components (Fig. 9.1C). Whether TBAB screens charges and/or changes the sign of the total charge on a particle and how this effect relates to the TBAB concentration remains as an open question for future research.

To visualise the effect of TBAB on the interaction strength between two charged colloids, we measured the pair interaction potential of the cationic-cationic interaction. We record three-dimensional positions in time at a low particle concentration using confocal microscopy and calculate the radial pair correlation function, $g(r)$. In a similar vein to the procedure outlined in chapter 4 we invert $g(r)$ to get the pair interaction potential, $U(r)$. The pair potentials for these systems is best described by a Yukawa potential. We do indeed find the expected effect, the interactions occur over much shorter lengths for higher TBAB concentrations (Fig. 9.1D). However, we can not make any conclusion about the possible charge inversion effect of TBAB as this was a simple system consisting of just one particle species.

With TBAB we have some control over the interaction strengths in our ionic colloidal system, whether this is through screening or charge inversion. However, the equilibrium state would still be a crystalline packing. To make a true ionic glass, we need additional control parameters. An easy way to avoid the formation of an ionic crystal is the addition of another cationic particle with a different size compared to the already present cationic particle. In analogy to glasses made from colloidal hard spheres, we can use this asymmetry in size to disrupt the formation of a crystalline lattice [6]. Such methods can be found in the atomic ionic glasses in the $(\text{Ln}, \text{Zr})\text{F}_{3+x}$ family [7]. Furthermore, the number ratio between anionic and cationic particles is also of high importance. A highly skewed ratio tends to promote the formation of an ionic glass [6]. We tested the latter method and found that it indeed yielded amorphous ionic packings (Fig. 9.2).

Figure 9.2 — Amorphous ionic packing as the result of a sample with a skewed number ratio between cationic and anionic particles. Cationic particles are large and coloured fuchsia, while the anionic particles are small and coloured yellow.

Strong and Fragile Glasses

The simulation model we introduced in chapter 7 for the study of microgels helped us to elucidate an outstanding question regarding the fragility of the colloidal glass transition. Experimental work had suggested that the microscopic origin of fragile and strong glass transitions in colloids is determined by the softness of the particles; softer particles have a stronger glass transition [9]. This would be an interesting finding as it would provide a possible way to study strong glass transitions with colloids that up to that point had all been found to undergo fragile transitions.

However, recent theoretical work suggests that the observed strong transition in these highly deformable microgel particles was not a real effect but only a result of plotting the data against the wrong parameter!

Figure 9.3 – Overview of the connectivity model of fragility in glasses. The range of variation in particle connectivity numbers, Δz is directly related to the fragility of the glass transition of such a system. For systems with a high spread in z , $\Delta z > 0$ the model predicts a fragile transition, while in the limit $\lim_{\Delta z \rightarrow 0}$ a strong transition appears. Colloidal glasses of spherical isotropic particles have a Δz in the range 11–16 and show fragile behaviour, whereas network glasses such as SiO_2 have very little variation in their coordination numbers, $\Delta z = z_0$, and show the corresponding strong transition. Figure reproduced with permission from [10]

Microgel particles are known to shrink as a response to an increase in osmotic pressure at higher concentrations. This makes it difficult to experimentally determine the proper volume fraction, ϕ , of the system. As an alternative the interpolated volume fraction or packing fraction, ζ , is used. This parameter does not account for shrinking of the particles and can therefore take values above unity. The theory showed that when the measured relaxation data would have been plotted against the real volume fraction, all samples, irrespective of their particle softness, would follow the same fragile glass transition.

With the help of our model we confirmed this theoretical finding; when plotted against ζ we observed transitions with different fragility indices. However, when we plotted our data against the real volume fraction, all curves collapsed onto a single fragile transition curve, as expected. This result shows that the *colloids as big atoms* paradigm does not always hold and much care is needed in the determination of the correct parameter to plot our data against. Our findings raise several questions: (i) what is the microscopic origin of the strong to fragile transitions? (ii) is it possible to capture this effect in the colloidal world via a different mechanism?

The leading theme through all research concerning glasses in this thesis has been the connectivity of load bearing bonds between particles in our systems. Could it be the case that the explanation for fragile and strong glass transition can also be found in relation to the coordination number, z , of the constituent particles. Strong glasses, such as those

formed by SiO_2 have a distinctly different topology compared to colloidal glasses formed by isotropic spheres, which form fragile glasses. The former is a network glass and as such has a well defined and fixed coordination number for every particle. For isotropic particles there is a wider distribution, $P(z)$, in the system. A theoretical prediction for the fragility index of the glass transition based on the probability distribution of coordination number, $P(z)$, has been made [10]. Assuming a Gaussian shape for $P(z)$, it was found that:

$$\tau \sim \exp \left\{ \frac{1}{4} \left(\frac{z_0}{\Delta z} \right)^2 \frac{T_0}{(T - T_0)} \right\} \quad (9.1)$$

which is the Vogel–Fulcher–Tammann equation with an explicit prefactor, $\frac{1}{4} \left(\frac{z_0}{\Delta z} \right)^2$, based on the width of the distribution of coordination numbers, Δz around the mean, z_0 .

To arrive at this equation the author made a similar assumption as we did in chapter 4: the relaxation time of a particle in a glass follows Arrhenius law with an energy term which is dependent on the particle's coordination number: $\tau \sim \exp(E(z)/k_B T)$. In amorphous systems, both the energy of the system E and the coordination number per particle are random numbers. If we assume Gaussian distributions for both random variables we can get the ensemble averaged relaxation time, $\tau(T)$, by integration over the probability distributions of E and z . Further simplifications lead to the result of equation 9.1. A complete derivation can be found in [11].

Based on equation 9.1, systems with a low Δz , such as network glasses, follow a stronger glass transition. Whereas liquids of hard spheres with $\Delta z \approx 4$, have a fragile glass transition (Fig. 9.3).

To test this theory in experiments we need methods of synthesising colloids with an anisotropic shape or interaction. Furthermore, we need the ability to control their interactions in such a way that we have full control over their coordination numbers. The synthesis of large batches of anisotropic monodisperse particles in bulk still remains a challenge. However, recent development have definitely brought us further towards the synthesis of colloids with very specific interactions in bulk. Their interactions are managed either through the use of specifically interacting patches [12] or through the use of DNA attached to their surfaces [13, 14].

Simulation methods can help us here; the digital creation of arbitrary particle shapes is facile. There exists simulation work on the glass transition of different polyhedra that found a different fragility for the different shapes simulated [15]. In this work, the researchers simulated octahedra, triangular cupolas, and tetrahedrons and compared those with the results for hard spheres. These shapes had different fragility indices, from strongest to most fragile: tetrahedron, triangular cupola,

Figure 9.4 – Glass transition for systems consisting of different polyhedra (right hand side, from top to bottom): octahedron, triangular cupola, and tetrahedron, in comparison with data for hard spheres. Shapes which have more local ordering and thus less variation in the probability distribution of coordination numbers exhibit a stronger transition, in agreement with the ideas outlined in the text. Figure reproduced with permission from [15]

octahedron, and spheres. The strongest of these, the tetrahedra and cupola, are able to form locally ordered clusters. The formation of local order decreases the variation in coordination number, this simulation finding is in agreement with the ideas outlined above. In the ensemble average there still is quite a large variation in coordination number, but the presence of local order lowers the spread with respect to a system of hard spheres.

Unfortunately, it is unlikely that shape alone can lead to a strong colloidal glass transition. Shapes that have a strong preference to form local order, such as cubes, also crystallise and do not have a glass transition in a monodisperse system. While the local ordering due to anisotropic shapes can make the glass transition stronger, we hypothesise that fully anisotropic and specific interactions are needed to make strong colloidal glasses.

Dynamics of Confined Systems

In chapters 2 and 3 we studied the dynamical behaviour of interstitial dopants in weak crystals and found that their dynamical behaviour is ultimately the result of the surrounding matrix particles. The difference between diffusion rates of dopant through perfectly ordered crystalline matrices versus weak disordered lattices is pronounced. We found a decrease of two decades in diffusion constants for static versus dynamic matrices. The same is true for the clustering between dopants that we observed. The attractive interactions between dopants emerge from the lattice distortion the dopants incur. These emergent effects lead to clus-

Figure 9.5 – Crystals of monodisperse repulsive Yukawa PMMA particles, diameter $d = 4 \mu\text{m}$, inside wells with a diameter of $30 \mu\text{m}$ in SU-8 fabricated using standard softlithography techniques. The use of optical tweezers gave us full control over the number of particles, N in every cell: $N = 6$ (A), $N = 9$ (B), $N = 10$ (C), $N = 11$ (D), $N = 12$ (E), and $N = 14$ (F). (G) We extend the experiments with Brownian dynamics simulations using the same parameters as in chapter 2 and find the relation between the total number of particles N and its division into shells. Here, n_0 is the outer most shell (red circles), n_1 the next shell in (blue triangles), and n_2 is the inner most shell (green squares). Filled symbols indicate data from simulations confirmed with experiments, while open symbols indicate only simulation data.

tering and at higher concentrations phase separation of dopant droplets (chapter 3).

Both of these findings have made it clear how important the immediate surroundings are for the dynamical behaviour of a colloidal particle. In fact, the dopants we studied can be interpreted as an example of a colloidal system under strong confinement. The dopant particles are confined by the presence of matrix particles with a marked difference between static versus dynamic and disordered confinement. In the case of a static base crystal the dopant particles experience a ‘leaky’ confinement. There are a number of escape paths from its current confined positions; it can hop from one interstitial site to the next. This is especially true for tetrahedral interstitial sites in a bcc lattice as these interstitial sites form a connected network (chapter 2 & 3). Thus, the dopants are confined to the volume of the network of interstitial sites when the base crystal is static. As soon as the confinement becomes dynamic at the frequencies relevant for interstitial movement, the dopants will on average experience fewer possibilities to escape their current confinement. Their effective confining volume decreases from the full network to a local cage. As a result their diffusion coefficient decreases dramatically upon dynamic confinement.

With the idea of the importance of confinement in mind we developed several colloidal systems with which to study confinement phenomena.

Figure 9.6 – Plots of the angular position, θ , for a single particle in every shell as a function of time on the radial axis. Shown for a system with $N = 14$ with conformation $[10-4-0]$ (**A & B**) and for a system with $N = 26$ with conformation $[14-9-3]$ (**C–E**). The outer most shell is always on the left hand side and the inner most shell on the right hand side.

We start with a two dimensional system of large PMMA particles, diameter $d = 4 \mu\text{m}$, confined to the bottom of a cylinder by gravity. Standard softlithography methods allow us to create confining cylinders with diameters ranging between $10 - 50 \mu\text{m}$ in SU-8. With the use of an optical tweezer we can add and remove particles at will from the confinement; in this way we have single particle control over area fraction. We find that from $N = 6$ onward the particles start to form shells inside the confinement. Experimentally we were able to put 14 particles in a single confinement with diameter $d = 30 \mu\text{m}$ (Fig. 9.5A–F). We are able to extend this range with the help of Brownian dynamics simulations over $500 \tau_B$; the simulations are performed with similar parameters as those used in chapters 2 and 3. We restrict the particle movements to two dimensions and a cylindrical confining wall element which interacts with the particles according to the same Yukawa potential as the one which we apply between particles. The extended series follows the trend as shown in figure 9.5G; from $N = 6$ to $N = 14$ the simulations give the same configurations as in experiments. We find a single shell at $N = 6$; addition of a single extra particle starts a secondary shell. The two-shell configuration stays intact until $N = 18$ when a third shell is introduced.

We are first and foremost interested in the effect of confinement on the dynamical behaviour of the confined particles. As a first attempt to visualise this effect we plot the angular displacement, θ , for a single particle in every shell as a function of time. As we are working in a circular system we plot this on a polar set of axis where the radial axis represents the simulation time (0 to $500 \tau_B$) and the polar axis represents the angu-

Figure 9.7 – (A) The particle pair potential for different concentrations of PAG, measured after illuminating for 60 seconds. The solid lines are fits to a repulsive Yukawa potential. (B) Computer render of the particles crystallised on the interface between the aqueous and organic phase. Particles are colour coded according to their number of nearest neighbours. Particles with 6 neighbours are coloured dark purple, particles with 5 neighbours are light green, and particles with 7 neighbours are blue. (C) Chemical structure of the photoacid generator used in this study: 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine

lar displacement (Fig. 9.6A–E). For a system with $N = 14$, configuration [10 – 4 – 0], we find that particles in the inner shell show much higher frequency dynamics compared to particles in the outer shell (Fig. 9.6A & B). We find the same effect for a system with three shells, $N = 26$, configuration [14 – 9 – 3]. In that system the inner shell shows, similarly to the case of $N = 14$, the most dynamic behaviour. The middle shell follows and the outer shell again is the least dynamic. There is a clear decoupling of dynamical behaviour between shells. Each shell thus appears to behave as a unique microphase.

Our second system opens up the capability to study three dimensional spherical confined systems. We make emulsions of *cis*-decalin and cyclohexyl bromide (CHB) in a mixture of water and glycerol. The organic phase contains PMMA particles which coat the interface between the two fluid phases and fill the organic droplets. A similar system has recently been used to study dynamics in confined amorphous packings of colloidal hard spheres [16]. Our system differs in the fact that our particles have long ranged repulsive interactions and form crystals on the interface and in the bulk of the droplets (Fig. 9.7B & Fig. 9.8A–I). With this system we were not just interested in the behaviour of a confined weak crystal but also in the effect of the confinement on the phase transitions in the system. To that end we dissolved a photoacid generator (PAG) into the organic phase; here we use the non-ionic PAG 2-(4-Methoxystyryl)-4,6-bis(trichloromethyl)-1,3,5-triazine (Fig. 9.7C). This class of molecules can generate charges upon radiation with UV light. This effect allows us to switch from a strongly repulsive potential to an almost

Figure 9.8 – (**A**, top row) Three snapshots in time of an emulsion droplet with particles and PAG, before (I), shortly after (II) and 2 minutes after (III) illumination with UV light. (**B**, bottom row) Three snapshots in time of a superheated bulk crystal of PMMA particles with PAG in the solvent, all snapshots are after illumination with UV light for 60 seconds. (I & II) Partially melted sample and fully melted sample (III). The solid red line is an indication for the melting front. In all samples, both in confinement and bulk, the PAG concentration is saturated.

hard sphere potential with the flick of a switch (Fig. 9.7A).

We test the UV induced charge generation in a bulk crystal of the same PMMA particles in a *cis*-decalin and CHB mixture. After illumination with UV light for 60 seconds the sample becomes superheated — long ranged repulsion that stabilises the lattice disappears but the sample holds its crystalline structure for a while. We do not observe the eventual melting nucleation event, but we do see the melting front travel through our sample (Fig. 9.8B–I, II, & III). If we apply the same procedure to the emulsion droplets we find the same effect when we illuminate for 60 seconds: the internal structure of the droplet melts (Fig. 9.8A–I & II). However, the system keeps evolving and surprisingly forms a confined colloidal gel. Because of this serendipitous behaviour we now not only have a system with which to study confined melting but also confined gel formation.

The study of confined dynamics is not only of importance for fundamental research into soft condensed matter but also for biologists. Many cellular processes are influenced by the high concentration of proteins inside cells. The crowding effectively allows for an additional form of compartmentalisation and process control [17, 18, 19]. Also for proteins themselves confinement is important; many proteins are stabilised by confinement effects [20]. During the folding process of proteins, confinement also plays an important role. Small containers, themselves proteins, called chaperones provide a small container that helps many proteins to fold into their active configuration [21]. The confinement of an unfolded protein in a chaperone effectively smooths out its potential energy landscape of folding; for a given energy E of the folding protein, the

confinement reduces the entropy S . The reduction in entropy promotes folding into the desired and biologically active conformation [22].

It is not just the interior of cells which are influenced by the effects of confinement: large ensembles of cells, such as biofilms, collectively show evidence of glassy dynamics [23, 24]. If we are to understand how cellular regulation is governed by mechanics at play in cells, it is essential to grasp the fundamental science behind dynamics under the influence of confinement.

Measuring Forces in Soft Condensed Materials.

Understanding the mechanical response of any kind of material on the single particle scales requires a method to measure the forces acting on those levels. However, just measuring forces acting between particles is not enough. Throughout this thesis we have encountered disorder on the single particle scale. The reality is that measuring the force on a single spot in the sample might not be representative for other parts in the sample, a form of heterogeneity. Isolating two particles and measuring their interaction forces with the help of optical tweezers or atomic force microscopes is not enough to fully understand the material. Especially when, due to the large number of particles present, heterogeneities appear in dynamics or the force response. The solution is to not just to quantify but also to map the locations of the forces at play and to do this *in-situ*.

In chapter 8 we designed and made progress towards the creation of a colloidal systems capable of both measuring forces acting between its constituent particles and visualising the location in three dimensions and time via confocal microscopy. While we did not reach our set goal, we did lay the foundations for future work on this type of sensor. Specifically we encountered the issue of sensitivity.

Our force measuring colloids were not sensitive enough in experiments for us to measure forces. Simulations showed us that the cause for this likely lies with the grafting density of polymers. Lowering this could considerably increase the sensitivity of the sensor. Furthermore, our current measurement methods use intensities from confocal microscopy of both the acceptor and donor channels to calculate a relative FRET efficiency ratio on a per-pixel basis. While this method is easily to implement, it suffers from errors due to background intensities, photon noise sources, and bleed through between detection channels.

Figure 9.9 – **(A)** FRET donor lifetime image of a two dimension loose packing of colloidal FRET force sensors. The image is taken on a Leica SP8 in lifetime measurement mode. The photon correlation was done with a Becker & Hickl SPC-830 Time Correlated Single Photon Counting module. **(B)** Distribution of donor lifetimes measured in the sample. The two observable peaks correspond to background signal from dye free in solution (long lifetimes, $\tau \sim 3000$ ps, and from FRET in the polymer brushes on the particles' surface, $\tau \sim 1800$ ps.

A more appropriate way to measure FRET efficiencies is through the use of donor fluorescence lifetime, a quantitative method which can give the true FRET efficiency: An increase in FRET will lead to a decrease in the average lifetime of the donors as FRET offers the excited state an extra relaxation channel which competes with fluorescence. We have performed a small experiment to test the feasibility of lifetime based imaging for our system and found that it could work. The lifetime imaging was done on a sample with a low volume fraction of colloids sedimented to the bottom glass plane (Fig. 9.9A). The suspending media contained some free fluorophore so that we can get information on the base donor lifetime without any acceptor present. We found two clear populations in the distribution of lifetimes: one at short lifetimes, corresponding to the polymer coronas on the particles where baseline FRET takes place, and one at longer lifetime, corresponding to free donor molecules in solution (Fig. 9.9B). This sample did not contain any depletant. As such we do not observe a third population with even lower lifetime due to an increase in FRET at particle contacts. This would be an obvious next step.

While measuring forces in colloidal packings is challenging and of great use to the field, the bigger challenge lies in nature. The real challenge is to measure forces in a biological context *in-situ* and under physiological conditions. There are methods to measure forces between whole cells and on a single cell level in general [25], but the real interest lies with forces between functional protein groups inside cells. Methods to measure forces inside cell based on methods involving FRET have recently been employed with very promising results [26]. However, these sensors are constructed by cells themselves as they consist of a single protein combining two fluorescent proteins (donor and acceptor), a random coil like domain (the central spring), and on both ends a link to

the two proteins of interest. The sensor is therefore fully dependent on the properties of those proteins and their sensitivities to force. The 300 fN sensitivity found in systems of semiconducting polymers can not be reached in those fully biological systems [27]. The fluorescent proteins are fully dependent on their conformation which will at some force denature and lose its functionality; this effectively sets the maximum force the system can measure. Furthermore, there are issues with bleaching and there is the need to construct a new system for every possible application. We feel that semiconducting polymers, which are photostable and can form the backbone for a modular force measuring system, are the perfect candidate for the future of force measurements inside living cells.

Conclusions and Outlook

Disorder unquestionably plays a pivotal role in many processes. The process of understanding its many influences on physical processes has only just began. In this thesis we have explored several scenarios where disorder, whether structural, dynamic, or a combination of both, plays a role. We have explored colloidal glasses, doped systems, and glasses from compressible particles. This chapter served to put the research in this thesis in a wider context.

While this thesis has tried to answer some of the questions regarding disorder, all of this work has been done in the context of colloids. It will be necessary to test our findings on the atomic or molecular scale if we expect any impact on real world material science. The challenges here are many, not least of which is the much faster time scales involved. However, the simulations on doped systems were performed in the context of particles interacting with each other via a Yukawa potential. The results of those simulations should be applicable to other systems with that interaction type. For colloidal glasses with spatial disorder both in structure and dynamics one of the main questions remains whether it is possible to find strong-fragile behaviour as observed in the molecular world. This quest will require more advanced synthesis methods for colloidal particles with anisotropic shapes and interactions.

The field of disorder in colloidal systems will undoubtedly remain an active field of research in the foreseeable future as new synthetic methods open new doors to answer new questions and findings in the colloidal world start to be translated to the world of the living cell.

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SUMMARY

IN THIS THESIS we have investigated the effects of disorder on the dynamical and structural behaviour of various soft condensed materials. Our aim was to elucidate how disorder in its many guises breaks conventional rules. We have focused on the following three aspects of disorder: (i) structural disorder as found in glasses, (ii) the structural and dynamical disorder of weak crystals with interstitial dopants, and (iii) disorder both in the structure of the material and in the constituent particles themselves exemplified by glasses made from compressible microgel particles.

In **chapter 2** we investigated, with Brownian dynamics simulations, the behaviour of dopants in weak crystals. We found that the large instantaneous fluctuations in the base crystal, which are a result of thermal excitations, disrupt the potential energy field as experienced by the dopant particles. The result is a two orders-of-magnitude slowdown in dopant dynamics as compared to a situation where there are no thermal fluctuations in the base crystal. Furthermore, we observed an emergent attractive interaction of elastic origin between the otherwise purely repulsive interstitial particles: introduction of dopants strains the lattice; this added strain is minimised with agglomeration of the dopant particles. This results in clusters of locally highly mobile dopants. Our results give a microscopic picture of dopant dynamics in a weak crystal and illustrate why elastical theories fail close to a crystal's melting point.

The first chapter on doped weak crystals took place at relative low dopant concentrations. This raised the question how a larger dopant concentration would change the situation. We try to find answers to this question in **chapter 3**. We identify a complex phase diagram as a function of dopant concentration. This phase diagram shows several transitions: (i) we find a transition from a phase of homogeneously dispersed interstitial dopants into a phase of clustered dopants; (ii) as the concentration of dopants increases we observe fully phase separated pockets of liquid dopant phases; (iii) if we keep increasing the dopant concentration, the

local volume fraction inside the pockets exceeds the melting volume fraction of a pure dopant phase and we have pockets of meta-stable dopant liquids; (iv) finally the dopant pockets merge and our system ends up as a two phase system of separated dopant and base phases. Our result suggest that there is the exciting possibility to study solid-solid phase separation in experiments on the Yukawa PMMA system, a scenario that has remained elusive in the ‘colloids as big atoms’ approach.

In the following chapter, **chapter 4**, we shifted our focus from doped weak crystals to colloidal glasses. Using four-dimensional confocal microscopy we experimentally studied the dynamical behaviour of colloidal glasses made from purely repulsive PMMA particles. We observe the expected fragile super-exponential increase in relaxation times with respect to volume fraction. Based on these observations we searched for a microscopic theory that linked local structure to global dynamics. We explain this global rise in relaxation times with a microscopic model based on the lifetime of load-bearing bonds every particle experiences with its neighbours. We use the erosion rates of these bonds to construct a frequency dependent model based on the elastic shoving model for glasses. We find excellent agreement between our prediction based purely on experimentally accessible parameters and the observed global slowdown. Our findings are in direct agreement with the conceptual picture of fluidity and rigidity first proposed by Frenkel, and expanded on by Trachenko and Brazhkin, in which vitrification is a continuous transition in which the characteristic frequency at which rigidity emerges shrinks as the solid state is approached.

In **chapter 5** we strive to make our analysis methods from **chapter 4** accessible to experimental data from scattering experiments. Our model for the glass transition relies on knowing the lag-time dependent coordination number, $Z(\tau)$. In experiments on a single particle level this parameters follows straightforward from the data. However, scattering experiments do not have direct access to this parameter. Scattering experiments do have access to the intermediate scattering function, $F(q, t)$. Via the Vineyard approximation, $F_d(q, t) \approx S(q)F(q, t)$, and an inverse Fourier transform we gain access to the distinct van Hove function, $G_d(r, t)$. From there it is trivial to get $Z(\tau)$ via integration of the first peak in the distinct van Hove function. In this chapter we show the first verification of the validity of the Vineyard approximation in supercooled liquids.

Chapter 6 is the first chapter that focuses on the third type of disorder we study in this thesis, amorphous structures made out of compressible microgel particles. In this chapter we study the binary glass transition of a system composed of a microgel glass together with a variable sized polystyrene population of particles at size ratios: $a = 0.20$, $a = 0.37$, and $a = 1.44$. We study the relaxation dynamics in these binary systems with the

help of contrast variation multispeckle diffusing-wave spectroscopy. This optical technique allows us to separate the relaxation behaviour of the polystyrene tracers from the dynamics of the microgel matrix. For the smallest size ratio we find a complete decoupling in the dynamics of the two populations. According to theoretical predictions there should also be a decoupling at $a = 0.37$. However, we do not find this in our experiments. At this intermediate size ratio and at the highest size ratio there is an identical slowdown in dynamics between microgel matrix and polystyrene probes.

Chapter 7 looks deeper into strong glass transitions as observed with very soft microgel particles in experiments. Recent theoretical work has indicated that this experimental finding is not real but only the result of the use of an inappropriate parameter. Microgel particles are known to shrink at higher concentrations due to high osmotic pressures. This shrinking process means that there no longer is a linear relationship between concentration and volume fraction, ϕ . The experimental relaxation data was plotted against the interpolated packing fraction, ζ , instead of the real volume fraction ϕ , as the latter is difficult to measure experimentally. The theories predict that when that data would be plotted against the real volume fraction all glass transitions would collapse onto one fragile transition line.

We construct a Monte Carlo simulation model with which we can test the theoretical predictions without having to explicitly assume that particles (de-)swell. In our model particles make translation moves and (de-)swelling moves. Exactly as in the experiments, we find strong transitions if we plot our simulation data against ζ . However, plotting the same data against ϕ completely collapses the data. This confirms that the strong colloidal glass transition unfortunately remains unidentified. Finally we show that our model is also useful for the study of selective decompression of compressible particles in a packing of hard particles.

The last experimental chapter of this is a methods chapter, as we work towards the construction of a colloidal force sensor capable of quantifying contact forces and visualising their spatial configuration. As such, **chapter 8** forms a backbone beneath all previous chapters as the distribution of forces plays a major role in determining the properties of materials. We graft polymers, doped with a low concentration of FRET donors and acceptors, onto the surface of SiO_2 colloidal spheres, inspired by previous research on single-molecule force sensors based on FRET in conjugated polymers. As particles come in contact, the polymer chains on the surfaces of the colloids come into contact, compress or even interdigitate with high enough pressures. The resulting local rise in FRET moieties gives rise to an increase in FRET efficiency relative to the applied force between two colloids. Furthermore, we can easily visualise the increase in FRET efficiency via confocal microscopy. We design a syn-

thetic method to make the colloidal FRET sensors and perform proof-of-concept measurements. Aided with coarse grained Brownian dynamics simulations we investigate the effects of acceptor to donor number ratios and the effect of grafting density. We find that lower grafting densities result in higher sensitivities. The early experiments combined with the simulation investigations open the way towards further engineering of and research into the design of self-reporting colloidal force sensors.

Finally, in **chapter 9**, the general discussion, we place our findings in an expanded scientific context and give an outlook for future research into disorder in soft condensed matter.

LIST OF PUBLICATIONS

This thesis:

- Justin Tauber*, Ruben Higler* & Joris Sprakel, **Anomalous dynamics of interstitial dopants in soft crystals**, *Proceedings of the National Academy of Sciences*, **113** 48, 13660-13665 (2016)
DOI: 10.1073/pnas.1609595113
- Ruben Higler & Joris Sprakel, **Doping colloidal bcc crystals — interstitial solids and meta-stable cluster**, *Scientific Reports*, **7**, 12634 (2017)
DOI: 10.1038/s41598-017-12730-8
- Ruben Higler, Johannes Krausser, Jasper van der Gucht, Alessio Zaccone & Joris Sprakel, **Linking slow dynamics and microscopic connectivity in dense suspensions of charged colloids**, *Soft Matter*, **14**, 780-788 (2018)
DOI: 10.1039/C7SM01781B
- Ruben Higler & Joris Sprakel, **Apparent strength versus universality in glasses of soft compressible colloids**, *In preparation* (2018)
- Ruben Higler, Raoul Frijns & Joris Sprakel, **Decoupling of the binary glass transition observed with contrast variation multispeckle diffusing-wave spectroscopy**, *In preparation* (2018)

Other work:

- Jan Maarten van Doorn, Jochem Bronkhorst, Ruben Higler, Ties van de Laar & Joris Sprakel, **Linking particle dynamics to local connectivity in colloidal gels**, *Physical Review Letters*, **(118)** 18, 188001 (2017)
DOI: 10.1103/PhysRevLett.118.188001
- Ties van de Laar, Ruben Higler, Karin Schroën & Joris Sprakel, **Discontinuous nature of the repulsive-to-attractive colloidal glass**

transition, *Scientific Reports*, **6**, 22725 (2016)

DOI: 10.1038/srep22725

- Zhi-Kuang Tan, Reza Saberi Moghaddam, May Ling Lai, Pablo Docampo, Ruben Higler, Felix Deschler, Michael Price, Aditya Sadhanala, Luis M Pazos, Dan Credgington, Fabian Hanusch, Thomas Bein, Henry J. Snaith & Richard H. Friend, **Bright light-emitting diodes based on organometal halide perovskite**, *Nature Nanotechnology*, (**9**) 9, 687-692 (2014)
DOI: 10.1038/nnano.2014.149
- Felix Deschler, Michael Price, Sandeep Pathak, Lina E. Klintberg, David-Dominik Jarausch, Ruben Higler, Sven Hüttner, Thomas Leijtens, Samuel D Stranks, Henry J. Snaith, Mete Atatüre, Richard T. Phillips & Richard H. Friend, **High photoluminescence efficiency and optically pumped lasing in solution-processed mixed halide perovskite semiconductors**, *The Journal of Physical Chemistry Letters*, (**5**) 8, 1421-1426 (2014)
DOI: 10.1039/C7SM01781B
- Ruben Higler, Jeroen Appel & Joris Sprakel, **Substitutional impurity-induced vitrification in microgel crystals**, *Soft Matter*, (**9**) 22, 1421-1426 (2013)
DOI: 10.1039/C3SM50471A

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During my BSc thesis, in the field of developmental molecular biology, I had my first encounter with scientific research. After this period I was unsure whether or not I would ever continue in scientific research. The fact that you have just read my PhD thesis testifies to the fact that something fortunate must have happened. By sheer luck I enrolled in the 'Advanced Soft Matter' course, where I met Joris who showed me the beauty and challenges of Soft Matter research. Joris, I can't thank you enough for this and all the guidance and help during my time at PCC following ASM. Taking your course and listening to your motivating stories renewed my love for science. This thesis is a direct result of that course. Here I also want to thank Jasper for giving me the opportunity to do my PhD without a proper proposal or plan and giving me all the freedom I could possibly want. I especially want to thank you for always being calm and supportive during all those moments when we decided to switch topics and projects on a whim, which happened quite frequently during the last four years.

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OVERVIEW OF COMPLETED TRAINING ACTIVITIES

Discipline specific activities:

Dutch Soft Matter Meetings, The Netherlands (2014-2018)[†]
 Microscopic and Spectroscopic Methods in Food and Plant Sciences,
 Wageningen, The Netherlands (VLAG, 2014)
 American Physical Society March Meeting,
 San Antonio, TX, U.S.A (APS, 2015)[†]
 Physics @ FOM, Veldhoven, The Netherlands (FOM 2015)[†]
 Institute of Physics Soft Matter Meeting,
 Cambridge, UK (IOP 2015 & 2016)[†]
 Institute of Physics Soft Matter Masterclass,
 Cambridge, UK (IOP 2016)[†]
 CHAINS, Veldhoven, The Netherlands, (NWO 2016)[†]
 Multiscale Mechanochemistry & Mechanobiology, Berlin, Germany
 (Max Planck Institute of Colloids and Interfaces, 2017)[†]
 Physics @ Veldhoven, Veldhoven, The Netherlands (NWO 2018)[†]

General courses:

The Physical Chemistry and Soft Matter Journal Club (2014-2017)
 MATLAB Masterclass, Wageningen, The Netherlands (2015)
 Presenting with Impact (WGS 2017)
 Communication with the Media and the General Public (WGS, 2017)
 Dutch eScience Day, Amsterdam, The Netherlands (2017)
 Scientific Writing (WGS, 2018)

Optionals:

Weekly Group Meetings (PCC, 2014-2018)
 Preparation of Research Proposal (2014)
 Discussion and Implementation of Digital Jabjournal pilot (PCC, 2015)