New Insights into the Mechanisms of Crystallisation and Vitrification – a Dynamic Light Scattering Study of Colloidal Hard Spheres

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A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy of Physics

March 2009

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Que siempre ilumina mi camino en la oscuridad
Abstract

This thesis reports on a comprehensive experimental study of the collective dynamics of colloidal hard sphere suspensions. The main quantity measured is the coherent Intermediate Scattering Function (ISF) using a range of techniques based on Dynamic Light Scattering (DLS). The collective dynamics are measured as a function of scattering vector for volume fractions spanning from dilute samples, through the fluid phase and the metastable region, up until deep in the glass region. This work describes two major explorations: (i) the effect of volume of fraction on the q-dependency of the collective dynamics; and (ii) a study of the ageing processes in colloidal glasses. The present work is unique in the application of several advanced experimental techniques, and in the level of averaging that has been carried out, enabling a more sophisticated analysis than has previously been possible. This includes the characterization of non-Fickian processes and the determination of the current-current correlation function (CCCF) in the metastable fluid, and the quantitative characterization of the ageing process in the hard sphere glass. In addition, by combining aspects of the coherent and incoherent ISFs, this work also allows the expression of the collective dynamics in terms of the single particle displacement. The results show a dynamical change at the freezing point ($\phi_f$), which exposes the incapacity of the system to dissipate thermal energy via diffusing momentum currents, i.e. viscous flow. The structural impediments responsible for this, associated with dynamical heterogeneities, begin at the structure factor peak, and spread to other spatial modes as the volume fraction increases. Above the glass transition ($\phi_g$), structural relaxation becomes arrested at all spatial modes probed, i.e. flow is arrested. It is found that, following the quench, samples above the glass volume fraction approach some final “ideal” glass in an algebraic manner. However, although the long time dynamics exhibit ageing, the non-ergodicity factor, a measure of the average structure of the sample, does not show any significant ageing. This dynamical ageing process, decoupled from changes in the average structure, is identified with irreversible exchange of particles.
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the results of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

Vincent A. Martinez

March 12, 2009
Acknowledgements

I would like to thank my supervisors Gary and Bill for their outstanding help from the first day until the very last day with reading and correction of the thesis in a very short time. This work could not have been done without them. In particular, thank you Bill for so many fruitful discussions and your attempt to stimulate my thinking (not always with success ahahah!!!), sharing your passion for physics, and your Peugeot 504. Thank you Gary for letting me “harass” you everyday and for your hospitality. Thanks to Phil Francis for his technical expertise.

I also would like to thank all my mates from the physics department for their attempts to teach me the “Stralian” accent: Thomas, Terry, Tobias, Ryan, Ben, Des, Matt, Nemo, Aaron, Yusen and Gary. Thanks to Los Chupacabras, the futsal team of the physics department. Thanks for the beer sessions on Fridays, probably instigated and promoted by Gary!!! Thanks to the support of the geek fest team for your support in “killing” Des. Ahahah so geeky!!! Thanks for DonDon, the quickest, cheapest and best Japanese restaurant ever! Thanks to Igor Pro for performing thousands of operations in a few minutes and supporting my yelling during programming. Thanks to Aaron for the tackling of the Monster Bash pinball and for those fantastic “Water” sessions. Thanks to the Age Quiz to make me look ridiculous with the bloody French questions that I can never answer. Thanks to my great mates from Handball for the games on Sunday but especially for the third half at the Beer garden!!! Thanks to Yusen, Tonia and “el pequenio” Amaru for promoting the Mexican Vibe. Thanks to Anthony for these memorable crazy art sound performances. Thanks to my parents, uncle and brother for their constant support!!! Finally but most important I would like to thank “mi chaparrita” to give me love. This is not only the end of a thesis but also the end of my Aussie adventure (for now).
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Chapter 1. Introduction

Upon quenching, by decreasing the temperature or increasing the density, a liquid can experience a transition to a crystalline solid. The temperature at which this occurs is called the freezing point $T_f$. Alternatively, depending on the quench depth and the fluid’s complexity, a liquid can instead form an amorphous solid, called a glass. This phenomenon is called the glass transition or vitrification, and the corresponding transition temperature is the glass transition temperature $T_g$, which depends on the cooling rate. At temperatures below $T_f$, but prior to the formation of one of these solid phases, the liquid is said to be supercooled or undercooled [1, 2].

Thermodynamically, the freezing transition is characterised by a discontinuous change in thermodynamic quantities when going through the transition from the supercooled liquid to the crystalline solid – the crystal has lattice planes that the liquid does not – and is classified as a first order phase transition [3]. By contrast, a glass is structurally almost indistinguishable from its corresponding supercooled liquid, despite the fact that glasses behave as solids - they have lost the ability to flow, and can withstand finite stress. While crystals have both short and long range order (or lattice planes) and are in an equilibrium state, glasses have no long-range order (no lattice planes) and are in an out-of-equilibrium state. This means that glasses evolve continuously in time without reaching an equilibrium state, even over very long time scales. Nonetheless the glass transition is characterised in many different ways. Thermodynamically, singularities are observed in the heat capacity and thermal expansion coefficients when traversing the glass transition temperature, and so the glass transition is often described as a second order phase transition. Kinetically, the glass transition is characterised by a dramatic slowing of the dynamics, characterized via a sharp (many order of magnitude) increase in the viscosity over a small range of temperatures around the glass transition, whereas no change is observed in the static structure factor (between the supercooled liquid and the glass). Through the temperature-dependence of the viscosity, Angell [4] identified two types of glasses, classified as strong and fragile, depending on whether or not they exhibit an Arrhenius behaviour.
1.1 Microscopic pictures: the cage effect and dynamical heterogeneity

A microscopic picture of the dynamics of liquids, first introduced by Frenkel [5], is that atoms of a liquid move spontaneously from one cage, formed by neighbour atoms, to another. The time necessary to trap or cage the atoms increases, by either increasing the liquid’s density or decreasing its temperature, until reaching the point of solidification where atoms are permanently trapped in their respective neighbour cages. The nature of the solid, whether crystalline or amorphous, is not specified.

Later, Adams and Gibbs [6] offered a microscopic picture of vitrification by assuming the presence of independent cooperatively rearranging regions of particles in the supercooled liquid. They explained the kinetic observations in terms of the growing size of these regions, expressed in terms of their configurational entropy, when approaching the glass transition temperature $T_g$. They concluded that the kinetic properties of supercooled liquids near the glass transition can be explained in terms of its thermodynamic properties. Thus, Adams-Gibbs theory links the kinetic observations with the thermodynamic interpretation of the glass transition.

The concept of cooperatively rearranging regions (CRR), introduced by Adams and Gibbs, was further developed by Cicerone and Ediger [7], who introduced the term dynamical heterogeneity (DH), though Schmidt-Rohr and Spiess first experimentally observed a heterogeneous distribution of correlation times [8], and “transient heterogeneity” was previously observed by Hurley and Harrowell [9]. These DH were further observed, identified and quantified via simulation [9-13] and experiments [14-16]. For a review of DH see [17, 18]. These DH are seen as clusters, within which particle motions are dynamically correlated both in space and time. It has been found in the literature that the size of such clusters of particles significantly grows as the glass transition is approached [19-27]. The best known quantification of the DH is via the dynamical susceptibility calculated from a four-point correlation function introduced by Franz et al. [11-13]. The dynamical susceptibility displays a peak, which increases and shifts towards longer times as temperature decreases. The maximum of the peak is used as the correlation length. Evidence of DH is found in many numerical simulation [10, 23, 24, 28] and experiments [14-16, 26, 29-32]. Another suggested measure of DH is a measure of the deviation from the Gaussian behaviour of the probability distribution function of particle displacements [25].
Recently, van Megen et al. [33-37] observed the emergence of a negative algebraic decay of the long-time tail of the Velocity Autocorrelation Function (VAF), from both DLS experiments and molecular dynamics simulation. This behaviour is incompatible with the positive long time tail of Alder [38], which is characteristic of momentum diffusion, and was interpreted as a signature of the presence of DH. They found that this dynamical anomaly occurs at the freezing point and so concluded that the onset of DH should be associated with the first-order transition.

The interpretation proposed by Götze et al. [39-41] relates the glass transition to kinetic or dynamical behaviour rather than thermodynamics. They developed the mode coupling theory (MCT), first used to describe critical phenomena and non-linear behaviour, and later used to describe the glass transition. MCT theory is based on a delayed, non-linear, coupling between density fluctuations on all spatial scales, and contains information about the system structure through the static structure factor S(q) (measured or calculated), and allows for predictions of dynamics through, for example, the density correlation function or Intermediate Scattering Function (ISF). MCT identifies a singularity at a critical temperature T_c. At T<T_c, the ISF undergoes a full decay, characteristic of an ergodic system while for T>T_c the ISF does not fully decay to zero and shows a plateau exposing the dynamical arrest of the system, characteristic of a non-ergodic system. Thus, MCT identifies the GT as a transition between ergodic and non-ergodic states. From the ISF (in particular the self ISF), the particle mean-squared displacement (MSD) may be calculated. The predictions of MCT are consistent with experimental results for colloidal hard sphere (HS) systems [37, 42-44] and with numerical simulations [45]. Despite this, MCT remains controversial, mainly due to a lack of a clear understanding of the physical interpretation of the theory, but also because MCT does not include ergodicity-restoring processes. Specifically, MCT does not predict the non-stationary behaviour observed in colloidal glasses [46-50]. The question that can be asked is, does MCT omit some processes which are important in a more complete understanding of the glass transition?

The cage picture, from Frenkel [5], suggests that the dynamical arrest of the glass predicted by the MCT is due to phenomena of length scale comparable with the interparticle distance, which contrasts with the picture involving dynamical heterogeneities. However, further studies [20, 21] have connected the DH with the cage picture of the MCT by identifying a change in the dynamical susceptibility in a time window corresponding to the plateau of the ISF, where deviations from diffusive behaviour is the most strongly exposed. As a
consequence, this work suggested that the cage picture should be modified to include both short range motion in the cage and cooperative rearrangement of the particles that eventually leads to escape from the cage.

It is believed that these dynamical heterogeneities are responsible for the dramatic slowing of the dynamics at the sharp glass transition due to a growing dynamical correlation length, observed for the dynamical susceptibility via a four-point correlation function. The growth of the size of these domains is now believed to be the driving mechanism for the increase in the viscosity or relaxation time – and thus DH is a key problem of the liquid-glass transition [51]. Most of the work to date has aimed to observe or characterize dynamical heterogeneities. However, while this work has provided insights into the microscopic mechanisms by which particles move upon approaching the glass transition, the nature of the heterogeneities, including the mechanisms for stress relaxation, remain unclear [52].

1.2 Colloidal hard sphere systems

To address these issues experimentally, we use a well-characterised system: colloidal particle suspensions with hard-sphere like interactions. Colloids are much bigger than atoms and so they can be observed either by microscopy or light scattering techniques. Because they are much bigger, they are also much slower than atoms and so the metastable state can be studied in real-time. Moreover, the dynamics of colloids are overdamped, and so under normal circumstances activated processes are expected to be suppressed.

That the assembly of equal-sized hard spheres exhibits a first order transition was first established via computer simulation by Alder and Wainwright [53, 54]. The equilibrium phase behaviour is well known [55] and only depends on the volume fraction, \( \phi \), of the particles in the sample, defined as the ratio of the particle’s volume to the sample volume (see section 3.1.4 for further details). Computer simulations [55] predict the coexistence of a fluid phase and a crystal phase in thermodynamic equilibrium between \( \phi_f = 0.494 \), and \( \phi_m = 0.545 \).

Experimentally, suspensions of colloidal particles with hard-sphere like interactions, such as PMMA particles sterically stabilised by PHSA, have confirmed the equilibrium phase behaviour of the hard sphere system [56, 57]. In addition, a glass transition has been identified at \( \phi_g \approx 0.565 - 0.57 \) [58, 59]. For \( \phi < \phi_g \), the crystallisation process occurs at homogeneously distributed sites through the bulk of the sample. By contrast, for \( \phi > \phi_g \), the bulk of the sample remains amorphous, and crystallisation occurs only at the meniscus and/or
wall of the samples; i.e. crystal growth is heterogenous in nature [59]. This is illustrated in Figure 1.1 and further details can be found in [56, 59]. In addition, the hard sphere nature of the interactions was confirmed through independent experiments [57, 60, 61].

Dynamic Light Scattering (DLS) experiments allow the measurement of the dynamical properties of these colloidal suspensions via the Intermediate Scattering Function (ISF). Dynamical arrest is found, for $\phi > \phi_g$, where the ISF does not fully decay in the experimental time window [58]. The results of such experiments were found to be in good agreement with MCT [37, 42, 43].

![Figure 1.1](image.png)

Figure 1.1: Experimental phase behaviour of colloidal suspensions with hard-sphere like interactions. Image courtesy of Pusey and van Megen [56].

### Ageing of colloidal systems

Unlike the thermodynamically equilibrated crystal, glasses exhibit ageing - slow, non-stationary dynamics [46], effected through rare, intermittent structural re-arrangements [62]. Work over the last decade has shown that amorphous soft matter exhibits significant ageing behaviour. Foams, colloidal gels and glasses, and clays such as laponite, all exhibit ageing behaviour [29, 46-50, 62-91]. Despite the diversity of these soft solids, their dynamical behaviours, exposed through measurements of the ISF, all show similar trends. The ISF is generally found to decay in two stages: an initial decay onto a plateau, followed by a final age dependent decay. The plateau height, which is indicative of the materials’ elasticity, is often observed to be non-stationary [62, 80, 89].
The ageing characteristics of these materials are also complex and sample dependent [76]. For laponite glasses, for example, two ageing regimes have been observed by some workers: an initial exponential ageing process, followed by a “full” ageing regime, where the ageing is a linear function of waiting time [75]. Recent work has suggested that the exponential regime is related to the liquid-glass transition upon cessation of shear, rather than true ageing of the glass [92]. By contrast, other workers have found power law ageing with exponents of order ~1.8 [77].

Another system where ageing has been observed is that of attractive hard spheres [80], where ageing was found to be very complex, with ageing continuing for up to ten days. Systematic studies of the ageing process in these systems are yet to be carried out. Clearly, however, ageing in all of these systems is yet to be fully understood.

Although suspension of hard sphere particles are simpler than many of the systems studied, only a handful of ageing studies have been carried out on hard spheres to date. To our knowledge there have been three confocal microscopy studies – two on a one-component colloidal glass [47, 49] and one on a binary colloidal glass [50], which showed that the mean-squared displacement exhibits significant ageing, but that there is little correlation with structural changes. From a light scattering point of view, since the first observation of ageing behaviour in a hard sphere glass [46], to our knowledge the only study is that of El Masri et al. [48]. In this work ageing was studied in measurements of the intensity correlation function, and it was found that the relaxation times measured for high volume fractions showed ageing at early times, with a possible plateau at later waiting times.

**Effect of polydispersity**

In practice, identical sized colloidal particles cannot be manufactured. Colloidal suspensions always contain a range of particle sizes around a mean value. This range is usually referred as the polydispersity, and its magnitude affects the crystallisation process and the equilibrium phase boundaries. Bolhuis and Kofke [93] established a volume fraction versus polydispersity phase diagram for hard sphere systems via computer simulation. They found complex phase behaviour, with fractionation or segregation occurring at high polydispersity. Experimentally, Henderson et al. [94] observed this fractionation through the presence of particles in the extremities of the particle size distribution (PSD) which were not incorporated into the crystals. Recent calculations of the equilibrium phase diagram for polydisperse hard spheres show a complicated structure for \( \sigma \sim 0.05 \), which includes multiple crystal phases with
different lattice parameters [95]. Recently extensive experimental studies have established that nucleation and crystallization processes are highly sensitive to small changes in the polydispersity [96-101]. Finally, Williams et al. [102] showed, using binary mixtures, that a high polydispersity restores ergodicity and melts the glass. Clearly the phase behaviour of a polydisperse system is more complex than that of a monodisperse hard sphere system. Moreover, there is evidence that a system of perfectly identical hard spheres does not have a glass transition [103].

1.3 Aims of this thesis

As pointed out by Anderson: “the deepest and most interesting unsolved problem in solid state physics is probably the theory of the nature of glass and the glass transition” [104]. Despite numerous studies over about the last two decades, the microscopic mechanisms or processes behind the glass transition are still poorly understood [105]. The overall aim of this thesis is to identify the mechanisms/processes whereby crystallization is frustrated, leading to a glass transition.

To do so the collective dynamics of colloidal hard sphere suspensions will be measured using dynamic light scattering (DLS). Experiments will concentrate on scattering vectors around the main peak of the (fluid) structure factor, and volume fractions spanning from the fluid phase up to deep in the glass region. The present work takes advantages of improved experimental techniques to conduct a comprehensive study of the dynamics of hard sphere suspensions. As well as using improved techniques, the current work is unique in the level of averaging that has been carried out in order to obtain data which is not only statistically valid, but is capable of withstanding the sophisticated analysis to be conducted. In addition, by combining aspects of the coherent and incoherent (or self) intermediate scattering functions (ISFs), this work allows the expression of the collective dynamics (the particle number density fluctuations) in terms of the single particle displacement (mean-squared displacement).

In particular, this thesis aims to address the following questions:

- Do the collective dynamics exhibit a dynamical anomaly, or qualitative change of dynamics, at \( \Phi_f \), as has been observed previously for single particle dynamics through experiment [33, 36, 106], MCT [37] and simulation [34, 35]?
- What are the mechanisms responsible for the dramatic slowing down of structural relaxation, and increases in the resistance to flow, that occur when a liquid is cooled below its freezing temperature?
To what extent are glass formation and crystallisation connected, as suggested recently by Shintani and Tanaka [51]? Is glass formation due to (or related to) the suppression or frustration of crystallisation? Is glass formation a consequence of the frustration of nucleation by complexity (e.g., polydispersity, asphericity etc.)?

Does ageing in hard sphere glasses have the same characteristics as ageing in other soft solids?

What are the mechanisms responsible of the ageing process, and does a colloidal glass reach stationarity?

1.4 Overview of the thesis

The basic theory of Dynamic Light Scattering (DLS) and an introduction to the dynamics of colloidal particle are presented in chapter 2. The experimental methods, including sample preparation, light scattering instrumentation, and the specialized procedures for measuring ergodic and non-ergodic media, are explained in chapter 3. Chapter 4 presents the results of collective dynamics measurements over the full range of volume fractions, and includes the comparison with single particle motion. Chapter 5 is exclusively dedicated to the study of the non-stationary or ageing behaviour of colloidal hard sphere glasses. Finally, chapter 6 presents conclusions and suggestions for further work.
Chapter 2. Light Scattering Theory

The experimental work in this thesis is mainly concerned with the measurement of the dynamics of concentrated colloidal hard sphere suspensions using Dynamic Light Scattering (DLS). I outline here specific theory necessary to understand the results, and the experimental methods used during this work will be detailed in chapter 3. In this work, the following conditions are always fulfilled: the scattering is elastic (or quasi-elastic); the particle size is comparable to the wavelength of the visible light; the refractive index of the particles have only a real part (no absorption); and the particles are closely refractive index matched to the suspending medium to limit the effects of the multiple scattering.

2.1 Static Light Scattering

Static Light Scattering (SLS) experiments are usually used to measure the single particle form factor $P(q)$ and the structure factor $S(q)$. The form factor $P(q)$ is simply the intensity of the light scattered from a single particle as function of the scattering vector $q$, and allows determination of the particle size distribution (PSD) defined through a mean radius $R$ and a polydispersity $\sigma$. The static structure factor $S(q)$ gives information about the reciprocal space distribution of the particles.

The average scattered intensity of $N$ identical spheres in the scattering volume in an orientationally invariant medium only depends on the amplitude of the scattering vector $q$, and can be written as

$$I(q) = N P(q) S(q) \quad \text{Eq. 2.1}$$

where $q$ is the amplitude of the scattering vector:

$$q = |q| = \frac{4\pi n}{\lambda} \sin\left(\frac{\theta}{2}\right) \quad \text{Eq. 2.2}$$

where $\lambda$ is the wavelength of the incident light source and $\theta$ is the scattering angle defined as the angle between the incident and scattered propagation vectors $\vec{k}_i$ and $\vec{k}_s$ as illustrated in Figure 2.1.
Figure 2.1: Optical path difference between secondary waves emitting from two points separated by a distance r in a particle. The secondary waves constitute the scattering light.

2.1.1 Form Factor

The form factor $P(q)$ describes the angular dependence of the scattered intensity of a single particle and depends essentially of the size, shape and refractive index of the particle. Two theories allows the calculation of $P(q)$: Mie theory and the Rayleigh-Gans-Debye (RGD) approximation. Both assume that multiple scattering is negligible. The theory of scattering by spheres of size similar to the incident light wavelength is called Mie scattering theory and requires a numerical solution to Maxwell’s equations. Mie scattering theory provides an exact calculation of a single particle form factor and details can be found elsewhere [107]. Under the conditions that: (i) particles are small relative to $\lambda$; (ii) particles and solvent have similar refractive indices; and (iii) absorption is negligible, Mie theory simplifies into the Rayleigh-Gans-Debye (RGD) approximation that provides a simple analytical expression for $P(q)$ for a homogeneous spherical particle of radius $R$:

$$P_{RGD}(q) = \frac{3}{(qR)^3} \left[ \sin(qR) - qR \cos(qR) \right]$$  

Eq. 2.3

2.1.2 Structure Factor

The main measure of the structure of an isotropic fluid is the radial distribution function $g(r)$, which describes the probability of finding two arbitrary particles separated by a distance r. $g(r)$ can be determined directly, for example by confocal microscopy, by marking the position of each particle. By contrast, static light scattering allows the measurement of the structure factor $S(q)$ defined as:

$$S(q) = \frac{1}{N} \sum_{j,k=1}^{N} \left\langle \exp[iq(\vec{r}_j - \vec{r}_k)] \right\rangle$$  

Eq. 2.4
The structure factor $S(q)$ is related to $g(r)$ and is simply its Fourier transform [108]:

$$S(q) = 1 + \frac{6\phi}{25q} \int_0^\infty [g(r) - 1] \cdot r \sin qr \cdot dr$$

Eq. 2.5

where $\phi$ is the volume fraction. A “simple” analytical expression can be obtained for $S(q)$ by “solving” the Orstein-Zernicke Eq. with the Percus Yevick closure applied for an equal-sized hard-sphere system. The expression and details are well referenced in the literature [108].

**Effect of polydispersity**

Laboratory prepared suspensions always contain a range of particle sizes around a mean value. This range is usually referred as the polydispersity of the particle suspensions. The mean radius, $R$, and polydispersity index, $\sigma$, together are usually a good approximation to the Particle Size Distribution (PSD) and both are obtained by applying numerical calculations from Mie theory and/or the RGD approximation to the experimental form factor $P(q)$. In this thesis these fits are carried out using Matlab programs written by G. Bryant [109].

The method of van Beurten and Vrij [110], which allows the calculation of the structure factor $S(q)$ for polydisperse hard-sphere systems, is used in this thesis. As we do not measure structure factors specifically here, the main purpose of this is to be able to determine where our measured scattering vectors are, relative to the peak of $S(q)$. Predictions of $S(q)$ are represented as functions of $qR$, in Figure 4.4 of chapter 4, for hard-sphere systems with a polydispersity of 8%. The position of the main peak identifies a length scale corresponding to the inter-particle distance. It is clear from Eq. 2.1 that the structure factor for a dilute suspension is equal to one as $P(q) \propto I_{dilute}(q)$. As the volume fraction increases, peaks appear and their shape (amplitude and width) and position change strongly with volume fraction.

**2.1.3 Multiple Scattering**

Multiple scattering occurs when a photon is scattered by particles more than once before leaving the scattering medium. As the interpretation of light scattering data relies on the knowledge of the scattering vector, multiple scattering means that the measured data will be corrupted by scattering from other angles or scattering vectors. Multiple scattering is strongly dependent on the difference between the refractive indices of the particles and the medium. As this difference increases the multiple scattering also increases. For the purposes of this thesis, two approaches are used to reduce, suppress and/or avoid multiple scattering. First,
multiple scattering can be reduced by closely matching the refractive indices of the particles and solvent medium. This is difficult, and only applicable to very specific systems. Even for low turbidity, contributions from multiple scattering are important where \( S(q) \) has a minimum, or for dilute suspensions at the form factor minima. To deal with this; multiple scattering can be suppressed by using Two-Colour Dynamic Light Scattering (TCDLS) [111]. The technique will be discussed in detail in section 3.2.1.

The effect of multiple scattering is similar to the effect of polydispersity, and causes a broadening of the minimum in the single-particle form factor. As a consequence, in order to not overestimate the polydispersity, it is important to remove any effect of multiple scattering when carrying out static light scattering measurements.

For a dilute suspension, the amount of single scattered intensity is lowest around the minima of the form factor, and contributions from multiple scattering will be greatest here. Thus it is crucial to use TCDLS for an accurate determination of the form factor. Special procedures using TCDLS, first done by Segre et al. [112], must be adopted and are detailed in the literature [109, 113].

### 2.2 Dynamic Light Scattering

Dynamic Light Scattering (DLS), also called Photon Correlation Spectroscopy (PCS), is a well-established non-destructive technique to measure the dynamics of colloidal suspensions. A brief overview is presented here, however further details of the technique can be found in the literature [114].

#### 2.2.1 Basics of DLS theory

A schematic for standard DLS is presented in Figure 2.2. A coherent light source of wavelength \( \lambda \) of the order of the particle size is focussed onto the sample. The incident light is scattered by the particles in the suspension and a detector measures the time-evolution of the far-field scattered intensity at a specific scattering vector \( q \). The region of overlap between the incident light and the detector optics is defined as the scattering volume \( V \) and, changes with the scattering angle.
Figure 2.2: Schematic showing the concept of DLS. As particles move through the sample, the scattered intensity, I(t), measured at a specific scattering angle, fluctuates with time. The scattering vector q is defined via the incident and scattered wavevectors, respectively k_i and k_s. The right schematic shows the change of scattering volume with the scattering angle.

The amplitude of the instantaneous scattered intensity $E(q,\tau)$, in the far-field limit, for an (amorphous) assembly of N spherical particles in a scattering volume V is

$$E(q,t) = \sum_{j=0}^{N} b_j(q) \exp[iq \cdot r_j(t)]$$  \hspace{1cm} \text{Eq. 2.6}

Where $r_j(t)$ and $b_j(t)$ are the instantaneous position and scattering amplitude of the $j^{th}$ particle, such that $P_j(q) = |b_j(q)|^2$. As the particles move in response to interparticle and thermal forces, their positions $r_j(t)$ change and the scattered intensity evolves in time. Thus the scattered light is seen as a random fluctuating pattern of dark and bright regions (“speckles”) of intensity $I(q,t) = |E(q,t)|^2$. Each speckle corresponds to a solid angle ($\lambda/V^{1/3}$) at the scattering volume V. As a consequence the far field scattered intensity measured by the detector fluctuates. The speed of these fluctuations is directly related to the particle dynamics.

In DLS one computes the normalised time-average autocorrelation function of the scattered intensity (IACF), $g^{(2)}_I(q,\tau)$:

$$g^{(2)}_I(q,\tau) = \frac{\langle I(q,t) I(q,t+\tau) \rangle_I}{\langle I(q) \rangle_I^2} = \frac{1}{N} \sum_{i=1}^{N} I(t_i) J(t_i + \tau) \left( \frac{1}{N} \sum_{i=1}^{N} I(t_i) \right)^2$$  \hspace{1cm} \text{Eq. 2.7}
where the brackets indicate the time average over a measurement time $T$ and $\tau$ is the delay time. DLS is performed under the following conditions: (i) the scattering volume contains a large number of particles $N$; (ii) the length of spatial correlations between particles is much smaller than the linear dimension of the scattering volume; and (iii) particles can move throughout the sample such that all possible spatial configurations are probed in the course of an experiment of reasonable duration. Under these conditions, from the Central Limit Theorem, the scattered electric field is a zero-mean complex random Gaussian variable [115]. Such variables factorise according to the following equation, commonly referred as the Siegert relation:

$$g^{(2)}_E(q,\tau) = 1 + c f(q,\tau)^2$$  Eq. 2.8

where $g^{(2)}_E(q,\tau)$ is the ensemble-average IACF, $c$ is the coherence factor, an experimental constant of order one determined by the ratio of the speckle area to the detector area, and:

$$f(q,\tau) = \langle \frac{E(q,t)E^*(q,t+\tau)}{\langle E(q)^2 \rangle_T} \rangle_T$$  Eq. 2.9

is the normalised field ACF or Intermediate Scattering Function (ISF). At low volume fractions, condition (iii) is fully respected, the system is termed ergodic and $g^{(2)}_E(q,\tau) = g^{(2)}_T(q,\tau)$. However at high volume fractions, for example in a colloidal glass, particles have restricted motions, and during the time of an experiment the system samples very few configurations, which are not fully representative of the system – in other words the time average is not equal to the ensemble average and $g^{(2)}_E(q,\tau) \neq g^{(2)}_T(q,\tau)$. In such circumstances, the sample is called non-ergodic, and special procedures must be adopted to probe the full dynamics of such a system [115]. Details of these methods are given in the section 3.2.2.

Assuming that a true ensemble average is obtained. Then, with Eq. 2.6, the field ACF is:

$$F_n(q,\tau) = \sum_{j,k=1}^{N} \langle b_j(q)b_k(q)\exp[iq \cdot (\vec{r}_j(\tau) - \vec{r}_k(0))] \rangle$$  Eq. 2.10

where $\langle \ldots \rangle$ indicate an ensemble average. The Eq. above is for the general case of a polydisperse system of spheres. For the special case where particles differ only in their scattering amplitude, the ISF can be separated into two components called the coherent ISF, $F_c(q,\tau)$, and the incoherent ISF (or self-ISF), $F_i(q,\tau)$ [116].
\[ F'(q,\tau) = \frac{b'^2}{N} F_c(q,\tau) + (\bar{b}^2 - \bar{b}'^2) F_i(q,\tau) \]  \hspace{1cm} \text{Eq. 2.11}

where \( \bar{b}'^n = \frac{1}{N} \sum_{j=1}^{n} b_j' q \) depends on the optical properties of the particle suspension. The coherent ISF, or first term of Eq. 2.11, is:

\[ F_c(q,\tau) = \frac{1}{N} \sum_{j,k=1}^{n} \left\langle \exp\left[i\mathbf{q} \cdot (\mathbf{r}_j(\tau) - \mathbf{r}_j(0))\right]\right\rangle \]  \hspace{1cm} \text{Eq. 2.12}

and describes the \( q^{th} \) spatial Fourier component of the particle number density fluctuations. We access scattering vectors in range \( 1 < qR < 5 \), that is a range of spatial scales that bracket the position, \( q_{\text{m}} R \approx 3.5 \), of the main peak of \( S(q) \).

The incoherent ISF, or second term of Eq. 2.11,

\[ F_i(q,\tau) = \left\langle \exp[i\mathbf{q} \cdot \Delta \mathbf{r}(\tau)]\right\rangle \]  \hspace{1cm} \text{Eq. 2.13}

is the moment generating function of the particle displacement \( \Delta \mathbf{r}(\tau) = \mathbf{r}(\tau) - \mathbf{r}(0) \). A cumulant expansion of the self-ISF allows the determination of the mean square displacement (MSD) of a single particle, \( \left\langle \Delta r^2(\tau) \right\rangle \) [117]:

\[ F_i(q,\tau) = \exp\left[-q^2 \frac{\left\langle \Delta r^2(\tau) \right\rangle}{6} \right] \left[1 + \frac{\alpha(\tau)}{2} q^2 \frac{\left\langle \Delta r^2(\tau) \right\rangle}{6} + \frac{\beta(\tau)}{6} q^2 \left(\frac{\left\langle \Delta r^2(\tau) \right\rangle}{6}\right)^2 + \ldots \right] \]  \hspace{1cm} \text{Eq. 2.14}

where \( \alpha(\tau) \) and \( \beta(\tau) \) are the non-Gaussian parameters. At low scattering vector, so that \( q^2 \frac{\left\langle \Delta r^2(\tau) \right\rangle}{6} \ll 1 \), the Gaussian approximation is valid and the MSD can be extracted from the self-ISF:

\[ F_i(q,\tau) \cong \exp\left[-q^2 \frac{\left\langle \Delta r^2(\tau) \right\rangle}{6} \right] \]  \hspace{1cm} \text{Eq. 2.15}

Both coherent and incoherent contributions can be probed separately. For identical particles, \( F^m(q,\tau) = F_i(q,\tau) \), and for a mixture of particles where the refractive index of one species can be adjusted so that \( b \rightarrow 0 \), then \( F^m(q,\tau) = F_i(q,\tau) \).
2.3 Schematic of the ISF

A schematic of the normalised coherent ISF,

\[ f(q,\tau) = \frac{F^m(q,\tau)}{F^m(q,0)} \]  
Eq. 2.16

from real data, is shown in Figure 2.3, for several volume fractions, \( \phi \), spanning from a dilute suspension, \( \phi \approx 0.01 \), up to a highly concentrated suspension, \( \phi > \phi_g \), corresponding to a colloidal glass. For a very dilute suspension of identical particles with random motion (Brownian motion), the positions \( r_i \) and \( r_j \) of the \( i^{th} \) and \( j^{th} \) particles are uncorrelated, and Eq. 2.11 and 2.16 simplify

\[ f(q,\tau) = \exp \left[ -q^2 \frac{\langle \Delta r^2(\tau) \rangle}{6} \right] = \exp[-q^2D_o\tau] \]  
Eq. 2.17

where \( D_o \) is the free diffusion coefficient defined by the Stokes-Einstein relation:

\[ D_o = \frac{kT}{6\eta R^2} \]  
Eq. 2.18

where \( k \), \( T \), \( \eta \) and \( R \) are respectively the Boltzmann constant, temperature, viscosity and particle radius. Exponential decay, represented by the lines in Figure 2.3, is associated with free particle diffusion, also called Markovian or Fickian processes (no inter-particle interactions). In other words, particles move freely and do not feel the presence of the other particles. Here and in the work to follow the delay time \( \tau \) is generally expressed in terms of the Brownian time \( \tau_B = R^2/6D_o \), the time required for a particle in this ideally dilute suspension to diffuse a distance equal to its radius.

When the volume fraction is increased, particles start to feel the presence of their neighbours (eg through particle encounters) and the processes responsible for the decay of density fluctuations are not fully diffusive anymore. Consequently, the decay of \( f(q,\tau) \) deviates from exponential. At a higher volume fraction, \( \phi=0.555 \) for example, we observe a clear shoulder, which separates fast and slow processes. The fast processes are commonly associated with local motion of the particle (intra-cage motion) and slow process with large-scale motion (escape from the cage). Finally, at \( \phi > \phi_g \), the ISF does not decay to zero in our experimental time window, which spans nine decades.
Figure 2.3: Schematic of the normalised ISF, $f(q, \tau)$, as a function of the delay time for several volume fractions, expressed in terms of the Brownian time $\tau_B$.

At $\phi < \phi_g$, the dynamics, quantified through $f(q, \tau)$, are independent of the waiting time $t_w$. The waiting time is defined as the starting time of an experiment following the quench – for the samples here this occurs when tumbling stops. For example, if we perform an experiment on day one and another experiment on day two, there would be no change in the dynamics, and so the ISF would be identical. However, for $\phi > \phi_g$, the dynamics show a clear dependency on the waiting time, as seen in Figure 2.3 for a volume fraction $\phi=0.584 > \phi_g$. This waiting time dependency, or non-stationarity, is called ageing. The non-ergodicity and non-stationarity properties of colloidal glasses make the measurement of the particle dynamics experimentally challenging, necessitating the several methods to be discussed in chapter 3.
2.4 Analysis of the Intermediate Scattering Function.

In chapters 4 and 5, we conduct experiments over a wide range of conditions, and analyse the coherent ISF in several different ways. Where possible, we also compare the data to measurements of the self-ISF. The analysis undertaken is described below.

2.4.1 The width function or mean-squared displacement

Another way to represent the data is to calculate the width function, which gives clearer exposure of the diffusive regime not seen in $f(q, \tau)$. Without loss of generality, the ISF can be written as

$$f_{s,c}(q, \tau) = \exp[-q^2 w_{s,c}(q, \tau)] \quad \text{Eq. 2.19}$$

where $f(q, \tau)$ and $w(q, \tau)$ are the ISF and width function respectively. The subscripts $s$ and $c$ refer to self and coherent, respectively. Thus the width function is simply calculated from the previous equation:

$$w_{s,c}(q, \tau) = -\frac{1}{q^2} \ln[f_{s,c}(q, \tau)] \quad \text{Eq. 2.20}$$

In the specific case of the self-ISF in the zero $q$-limit, the width function is directly related to the mean-square displacement (MSD), $\langle \Delta r^2(\tau) \rangle$:

$$w_s(q, \tau) \bigg|_{q\rightarrow 0} \langle \Delta r^2(\tau) \rangle/6. \quad \text{Eq. 2.21}$$

Short and long time diffusive behaviours

It is common to define short-time and long-time diffusive limits where the width function grows linearly with delay time. These processes are quantified through the short-time and long-time diffusion coefficients, respectively $D_s^i(q)$, $D_s^c(q)$, $D_L^i$, $D_L^c$.

$$w_s(q, \tau) \bigg|_{\tau \rightarrow 0} D_s^i(q) \cdot \tau \quad \langle \Delta r^2(\tau) \rangle \bigg|_{\tau \rightarrow 0} = 6D_s^i \cdot \tau$$
$$w_s(q, \tau) \bigg|_{\tau \rightarrow \infty} D_s^c(q) \cdot \tau \quad \langle \Delta r^2(\tau) \rangle \bigg|_{\tau \rightarrow \infty} = 6D_s^c \cdot \tau \quad \text{Eq. 2.22}$$

Where '0' and '∞' refer to the lower and upper limits of the experimental time window. For the specific case of a dilute suspension, $\phi \sim 0.01$, collective and self short-time and long-time diffusion coefficient are constant and equal to $D_o$:

$$D_s^i(q) = D_s^c(q) = D_L^i = D_L^c = D_o \quad \text{Eq. 2.23}$$
Crossover between short and long time behaviour

As the volume fraction increases, the processes responsible of the decay of the ISF are not fully diffusive and a separation between the fast and slow processes appears. The inflection point, at the crossover between the fast and slow processes, corresponds to the maximum deviation from a diffusive process. This crossover is identified by calculating the logarithmic derivative \( n_c(q, \tau) \) of \( w_c(q, \tau) \) or \( n_s(\tau) \) of \( \langle \Delta r^2(\tau) \rangle \):

\[
n_c(q, \tau) = \frac{d \log[w_c(q, \tau)]}{d \log \tau} \quad \text{and} \quad n_s(\tau) = \frac{d \log[\langle \Delta r^2(\tau) \rangle]}{d \log \tau}
\]

Eq. 2.24

Where an inflection point is observed in the width function (or MSD), a minimum is identified in \( n_c(q, \tau) \) (or \( n_s(\tau) \)). From the identification of this minimum, we can extract three quantities to quantify the crossover: the value of the minimum of \( n_c(q, \tau) \) and \( n_s(\tau) \), respectively \( \nu_c(q) \) and \( \nu_s \); the delay time at the minimum \( \tau_m^c(q) \) and \( \tau_m^s \); and the value of the coherent and incoherent ISF, respectively \( f_c(q, \tau_m^c(q)) \) and \( f_s(\tau_m^s) \).

\[
\nu_c(q) = \min[n_c(q, \tau)] = n_c(q, \tau_m^c(q))
\]

\[
\nu_s = \min[n_s(\tau)] = n_s(\tau_m^s)
\]

Eq. 2.25

\[\text{2.4.2 Time-dependent diffusion coefficient}\]

Another way to identify the short-time and long-time diffusion coefficients is to calculate the time-dependent diffusion coefficient:

\[
D_c(q, \tau) = \frac{d w_c(q, \tau)}{d \tau}, \quad D_s(\tau) = \frac{d \langle \Delta r^2(\tau) \rangle}{d \tau}
\]

Eq. 2.26

Here the short-time and long-time diffusive regime are identified where the time-dependent diffusion coefficient is constant with delay time, and so:

\[
D'_c(q) = \lim_{\tau \to 0^+} [D_c(q, \tau)], \quad D'_s = \lim_{\tau \to 0^+}[D_s(\tau)]
\]

Eq. 2.27

\[
D'_c(q) = \lim_{\tau \to \infty} [D_c(q, \tau)], \quad D'_c(q) = \lim_{\tau \to \infty}[D_s(\tau)]
\]

Eq. 2.28
2.4.3 Current-Current Correlation Function (CCCF) and Velocity of Autocorrelation Function (VAF)

The wave-vector dependent current-current correlation function $C(q, \tau)$ is defined as [108]:

$$C(q, \tau) = \frac{1}{N} \left\{ \sum_{i=1}^{N} \sum_{j=1}^{N} [\bar{q} \cdot v_i(\tau)v_j(0) \cdot \bar{q}] \exp \left[ iq \cdot (r_i - r_j) \right] \right\}.$$  \hspace{1cm} \text{Eq. 2.29}

Where $v_i(\tau)$ and $v_j(0)$ are the velocities of particle $i$ at $\tau$, and particle $j$ at $\tau=0$, respectively. $C(q, \tau)$ gives an insight into the collective correlations through the ability of the instantaneous velocity of one particle $i$ to subsequently influence the motion of its neighbours $j$. The CCCF can be calculated from the coherent ISF:

$$C(q, \tau) = \frac{d^2 F(q, \tau)}{d\tau^2}.$$ \hspace{1cm} \text{Eq. 2.30}

In the special case where $i=j$, the Velocity Autocorrelation Function (VAF), $Z(\tau)$, is defined and can be calculated through the self-ISF or MSD:

$$Z(\tau) = \langle v(0)v(\tau) \rangle = -\lim_{q \to 0} \frac{1}{q^2} \frac{d^2 F_s(q, \tau)}{d\tau^2} = \frac{d^2 \langle \Delta r^2(\tau) \rangle}{d\tau^2}.$$ \hspace{1cm} \text{Eq. 2.31}
Chapter 3. Experimental Methods

This chapter will introduce the experimental methods used to measure the particle dynamics of colloidal hard sphere suspensions. First, section 3.1 deals with the preparation of the particle suspensions and their characterisation. Specific procedures and DLS techniques for ergodic and non-ergodic media are discussed in section 3.2. Section 3.3 presents the general procedures for obtaining the ISF from the raw data.

Since the original observation of a glass transition in suspension of spherical colloidal particles by Pusey and van Megen [58], several improvements have been made on a number of levels: preparation of the particles, determination of the volume fraction, and improved experimental techniques provide improved accuracy and reproducibility. These improvements make possible the sophisticated analysis outlined in Chapter 2, and applied in Chapters 4 and 5.

3.1 Particle suspensions

3.1.1 Preparation

PMMA particles coated with PHSA [118] have become widely used as hard-sphere models both for light scattering and microscopy based experiments. Since the original observations of Pusey and van Megen [56, 58], there have been several improvements in the preparation of these particle suspensions. Originally carbon disulphide (CS$_2$) was mixed with decalin to provide better index matching. However CS$_2$ is very volatile and so evaporation occurs, making control of the volume fraction very difficult. As a replacement of CS$_2$, tetralin was used to improve the index matching and limit the evaporation. However, it was found that tetralin is absorbed by the particles (PMMA) over long times, causing not only a change in the particle size but also a discolouration, and changes in the index matching of the particle suspensions with, in particular, absorption. The use of copolymer particles provides good index matching in a single solvent, allowing good control of the turbidity (via temperature control [102, 113]), and low levels of multiple scattering, while allowing the samples to remain stable over years, with significantly reduced uncertainty in the volume fraction.

Particle suspensions used in the experiments reported in this thesis were prepared by S.M. Underwood. The preparations were extensively detailed in previous work [119] and are a modification of the original method of Antl et al. [118] based on emulsion polymerisation.
followed by a stabilisation processes. The particles consist of a copolymer core of methymethacrylate (MMA) with either trifluorethylacrylate (TFEA) or trifluorethylmetacrylate (TFEMA). The monomers TFEA or TFEMA are incorporated to achieve refractive index match in a single solvent (cis-decalin). This index matching (or optical matching) reduces the amount of multiple scattering. In particular, TFEMA provides a better index match than TFEA. The particles are sterically stabilised by chemically bonding a thin coating, approximately 10 nm, of poly-12-hydroxystearic acid (PHSA) creating a short-range steric repulsion between particles. After the polymerisation and stabilisation processes are completed, particles are transferred into the solvent decalin (cis+trans), before being transferred into cis-decalin. The hard sphere nature of the particle suspensions is confirmed during phase behaviour studies [57] and will be explained in section 3.1.4.

The particle size distribution, characterised by a mean radius R and a polydispersity $\sigma$, is determined by a combination of electron microscopy and SLS/DLS, providing very accurate particle size distributions. This is presented in section 3.1.3.

Figure 3.1: Schematic of a particle in suspension. Particles consist of a core of PMMA + copolymer with a shell of PHSA (not to scale). Particles are suspended in cis-decalin to allow a better index match and reduce the contribution of multiple scattering. Three particle suspensions with different core composition are used in this work. The core compositions are presented in Table 3.1.

3.1.2 Particle Suspensions

Samples were prepared at several volume fractions from three different stock suspensions. Each contains particles suspended in cis-decalin with a different core composition and particle size distribution (see Table 3.1). We adjust the volume fraction of the sample by either diluting (adding solvent) or concentrating (centrifugation + removal of solvent) the particle
suspension. Extreme care is taken to avoid any contamination from dust or residual chemicals. DLS studies in chapter 4 were performed on samples prepared from XL63 and in chapter 5 from XL52, XL63 and a binary mixture of XL52 and XL48.

<table>
<thead>
<tr>
<th>Composition</th>
<th>R (nm)</th>
<th>σ</th>
<th>D_o (nm².ms⁻¹)</th>
<th>τ_B (s)</th>
<th>Scaling Factor</th>
<th>Cell Name</th>
<th>Purpose</th>
</tr>
</thead>
<tbody>
<tr>
<td>XL63</td>
<td>MMA 61% MAA 5% TFEMA 24%</td>
<td>~ 185</td>
<td>8.9%</td>
<td>370</td>
<td>0.0153</td>
<td>1.224</td>
<td>w12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>w13</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>w14</td>
</tr>
<tr>
<td>XL52</td>
<td>MMA 79% MAA 5% TFEA 16%</td>
<td>~ 200</td>
<td>6%</td>
<td>345</td>
<td>0.0193</td>
<td>1.158</td>
<td>SA1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>XL48</td>
<td>MMA 61% MAA 5% TFEA 24%</td>
<td>~ 120</td>
<td>9%</td>
<td>575</td>
<td>0.0042</td>
<td>1.168</td>
<td>N/A</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
</tbody>
</table>

Table 3.1: Particle descriptions of the stock solutions used in this work. Values are extracted from [109, 113, 119]. Accurate measurement of the PSD of XL63 were performed during this work and results agree perfectly with those of [109]. D_o and τ_B are calculated for T=23°C.

Sample cells are made of glass and the dimension depends on the experiment. For DLS experiments we used cylindrical cells of diameter ~ 11mm. For the phase behaviour study, we used square cells of side ~10mm. Square side cell allows improved accuracy when measuring the crystal volume fraction during the phase behaviour study (see section 3.1.4). Both type of cells have screw type caps fitted with an approximately 1mm thick viton disc to avoid evaporation. All cells were thoroughly washed and cleaned with several solvents and acetone vapour prior to use.

### 3.1.3 Optical Characterisation

The optical characterisation has two main purposes. First it allows the determination of the particle size distribution (PSD), defined by a mean hydrodynamic radius R and a polydispersity index σ. Bryant et al. [109] did this in previous work by a combination of DLS and SLS techniques. Results are presented in Table 3.1 Another procedure to determine the PSD consists of using a Scanning Electron Microscopy (SEM) and taking pictures of thousands of particles. The image processing and analyses also allow the determination of the PSD. However it is a time consuming procedure, as thousands of particles must be probed to get reliable statistics [120]. For an illustration, a picture of an XL63 particle suspension is
presented below. Second, as detailed in [113], the particle core, adsorbed layer and suspended liquid are so closely optically matched that, not only the turbidity, but also the particle form factor is sensitive to the temperature. Thus the temperature-dependence of the form factor $P(q)$ can be used to optimise the index match. This is particularly useful for binary mixtures, where particles can be selectively optically matched [102].

![SEM picture of XL63 particles](image)

Figure 3.2: SEM picture of XL63 particles. Image processing and analyses allows the determination of the PSD via SEM.

In section 5.3, we study binary mixtures by introducing a small amount of particles with $R \sim 120\,\text{nm}$ (XL48) into a suspension of larger particles with $R \sim 200\,\text{nm}$ (XL52). Due to the difference in composition between XL48 (24% TFEA) and XL52 (16% TFEA), we can optically match either XL48 or XL52 with the solvent by tuning the temperature as illustrated in Figure 3.3. Under these conditions, DLS experiments allow the determination of the partial Intermediate Scattering Function $f_{11}(q,t)$ and $f_{22}(q,t)$, where indices 1 and 2 correspond to large (XL52) and small (XL48) particles respectively. Also by evenly matching both small and large particles, the partial $f_{12}(q,t)$ can be obtained. This has been done in previous work, and details can be found in the literature [102].

![Optical matching of a binary mixture of XL52 (large) and XL48 (small) particles by changing the temperature](image)

Figure 3.3: Optical matching of a binary mixture of XL52 (large) and XL48 (small) particles by changing the temperature.
Figure 3.4a presents the form factor $P(q)$ for XL52 and XL48 at one scattering angle as a function of temperature. The maximum contrasts in scattering from the two particle types is achieved at 6°C for XL52 and 26°C for XL48. At 15°C both small and large particles have the same scattering amplitude. For temperature control reasons, we choose to work at ambient temperature $T=23°C$. At this temperature the scattering amplitude of the big particles (XL52) is approximately 50 times the scattering amplitude of the small particles (XL48).

![Figure 3.4: Form factor $P(q)$ of XL52 (open squares) and XL48 (filled squares) as functions of temperature at a scattering angle $\theta=62°$ [113].](image)

### 3.1.4 Phase behaviour

The particles used here can be represented by a core-shell particle as illustrated in Figure 3.1. The shell corresponds to the PHSA coating around the particle core (PMMA+co-polymer), which solvates the suspending liquid and contributes to the “effective” hard sphere particle radius, and so to the effective particle volume fraction $\phi_{\text{effective}}$. The effective particle volume fraction $\phi$ is defined as the ratio between the volume of the particles $V_p$, where the shell contains liquid, and the total volume of the suspensions $V_T$.

$$\phi_{\text{effective}} = \frac{V_p}{V_T}$$  
Eq. 3.1

The volume of the particles corresponds to the volume of the core $V_{\text{core}}$ and the shell (coating) $V_{\text{shell}}$. In practice, it is difficult or impossible to determine with accuracy the small amount of liquid in the shell contributing to the effective particle radius. Therefore, for an individual suspension it is important to establish the phase behaviour, in order to map the observed
freezing volume fraction onto the well-known hard sphere system obtained by numerical simulation.

**Volume fraction of the stock solution**

First the particle and liquid mass fractions of the stock solution, respectively \( \omega^0_p \) and \( \omega^0_L \), are determined. Details about the procedure of the determination of the particle mass fraction are given elsewhere [121]. One drop of a stock is placed in a low vacuum oven at a temperature of 80°C for 24h. Then, the dried residue (particles) is placed for 5 min in a humidity controlled environment and then the mass is recorded, allowing the determination of the particle mass fraction of the stock solution \( \omega^0_p \) (containing particle core and shell with no liquid). Then, the core volume fraction is calculated from the particle mass fraction, using known densities of the particles and cis-decalin:

\[
\phi^0_c = \frac{\omega^0_p}{\omega^0_p + \frac{\rho_p}{\rho_s}(1 - \omega^0_p)} \quad \text{Eq. 3.2}
\]

**Phase behaviour study**

The phase behaviour study consists of identifying the observed freezing volume fraction, where crystallisation first occurs [57]. We use the procedure of Paulin and Ackerson [122], which takes into account corrections for sedimentation not considered in the original observations of Pusey and van Megen [56]. Results are shown in Figure 3.5.

Figure 3.5: Equilibrium phase diagram of XL63. Line is a linear fit to extrapolate the observed volume fraction at the freezing transition.
As seen in Figure 3.5, it is relatively easy to estimate the freezing core volume fraction. However, difficulties were found in identifying the melting core volume fraction, as the crystal fraction differs from one at high volume fraction. This can be explained by fractionation or segregation of some particles due to a relatively high polydispersity (~8-9%). This fractionation was predicted by Bolhuis and Kofke [93], via computer simulations, and was experimentally confirmed by Henderson et al. [94] through the presence of particles in the extremities of the PSD that are not incorporated into crystals. Clearly the phase behaviour at such polydispersity is more complex than the one-component hard sphere system. Thus mapping the observed freezing core volume fraction, $\phi_{i}^{\text{core}}$, onto the freezing volume fraction for the one-component hard sphere system, $\phi_{i}=0.494$, is a considerable simplification. An alternative would be to map onto the freezing volume fraction for a 8-9% polydisperse hard sphere system, $\phi_{i}=0.525$ [93]. However, in order to compare with previous work, we choose to map onto the one-component system.

The scaling factor $f = \phi_{i}/\phi_{i}^{\text{core}}$, obtained from the phase behaviour study, allows the determination of the effective volume fraction of the stock solution from the core volume fraction:

$$\phi_{\text{eff}} = \left( \frac{f - 0.494}{1 - 0.494} \right) \phi_{i}^{0}$$

**Eq. 3.3**

**Volume fraction of samples**

Samples are prepared from the stock solution and mass of stock solution, $m_{\text{stock}}$, in the sample is recorded. Then by adding or removing solvent of mass $m_{L}$, the effective volume fraction is changed and calculated via the following expression [121]:

$$\phi = \phi_{\text{eff}} = \frac{1}{1 + \frac{\rho_{\text{PMMA}}}{\rho_{c} m_{\text{stock}} \omega_{p}^{0}} \left[ m_{\text{stock}} (1 - \omega_{p}^{0}) + m_{L}^{i} \right]}$$

**Eq. 3.4**

Where $c = (f - 0.494)/(1 - 0.494)$ and $m_{L}^{i}$ can be either positive (dilution) or negative (concentration). Homogeneous crystallisation occurred in the bulk in a few days for effective volume fractions $\phi_{\text{eff}} < 0.563$ while no homogeneous crystallisation is observed in the bulk for months for $\phi_{\text{eff}} \geq 0.574$ – this is designated as the glass phase. At $\phi_{\text{eff}}=0.467$ and 0.478, sedimentation induced crystallisation is observed after a few weeks. However, the gravity free crystal fraction, e.g. after correcting the effect of gravity, is found to be zero. The phase behaviour of XL52 and XL48 have been studied previously [102] confirming the hard-sphere
behaviour of these systems. Values of the scaling factors for XL52, XL48 and XL63 are presented in Table 3.1.

Here our experimental value of $\phi_g$ is in the range 0.563-0.574. This is consistent with the range of $\phi_g = 0.56.5-0.58$ reported in previous experimental studies of hard sphere system either by observing a change of crystallisation mechanism [58, 59] or a dynamical “arrest” via DLS measurement [123] and confocal microscopy [124]. However, results of two recent studies contrast with previous work and the present results. Cheng et al. measured the low-shear viscosity of a “5% polydisperse” hard sphere suspension as function of volume fraction. They found an exponential divergence of the low shear viscosity at $\phi=0.64$ even though the last data point is at $\phi=0.58$ and measurement beyond this volume fraction was not experimentally possible. This study concluded that these data indicate no glass transition at or near $\phi=0.58$. Also a recent DLS study of ~10% polydisperse hard sphere suspension [125] shows no dynamical arrest up to $\phi=0.597$ and results beyond this volume fraction are not presented. In this study, it is mentioned that polydispersity is so high that no crystallisation is observed for months. As the phase behaviour cannot be used in such cases (no freezing transition or melting point), this study determines the effective volume fraction “by comparing the short-time self-diffusion coefficient measured by DLS and theoretical calculations giving uncertainties of about 5%.

In the present study, if we rescaled the volume fraction (based on theoretical results for 8-9% polydispersity), the freezing volume fraction would scale to $\phi=0.525$ [92], and the observed glass transition to $\phi_g=0.60-0.61$. As mentioned previously, the polydispersity plays an important role in the observation/determination of the disorder-order transition and the liquid-glass transition. Thus, extreme care should be taken when attempting to determine the volume fraction of the glass point.
3.2 Dynamic Light Scattering

We used several techniques, all based on DLS, to measure the particle dynamics of ergodic and non-ergodic media. Three different ALV DLS goniometers are used and are listed in Table 3.2.

<table>
<thead>
<tr>
<th>Setup</th>
<th>Light source (λ)</th>
<th>Detector(s)</th>
<th>Correlator (minimum τ)</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>HeNe (632.8nm)</td>
<td>2x APD</td>
<td>ALV6010 (6.5 ns)</td>
<td>Fast DLS (FDLS)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cross-correlation (removes dead time)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>Ar (488nm and 514nm)</td>
<td>2x PMT</td>
<td>ALV5000 (0.2µs)</td>
<td>TCDLS</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cross-correlation (suppress multiple scattering)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>HeNe (632.8nm) Ar (501nm)</td>
<td>PMT</td>
<td>ALV5000 (0.2µs)</td>
<td>PvM method Echo DLS</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Echo: NI board (1s)</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.2: ALV goniometers.

3.2.1 Dynamic Light Scattering for ergodic media

In the first setup, referred to as FDLS, a laser light (λ=632.8nm) illuminates the sample and Avalanche Photon Detectors (APD) measure the scattered intensity. The detected signal is separated into two signals $I_0$ and $I_1$ via two optical fibres containing the same signal $I_0 = I_1$, but $I_1$ is delayed via a fibre optic delay line. Then a cross-correlation of both signals $I_0$ and $I_1$ effectively removes the detector dead-time [126, 127] and reduces the lower-limit of the dynamic window to 6.5ns. APD has a better count detection efficiency at $\lambda=632.8$ nm than a standard Photo Multiplier Tube (PMT). Particle suspensions, which are well index matched (XL63), have low scattered intensity and the use of an APD for such systems is a considerable advantage at some scattering angles.

The second setup, referred to as TCDLS, is a state-of-the-art technique [112] that can be operated in (conventional) auto-correlation mode, or, for suppression of multiple scattering, in cross-correlation mode. In either case, the sample is illuminated by two independent laser beams, blue and green, of wavelength $\lambda=488$nm and $\lambda=514$nm. Two detectors measure the scattered intensity so that the scattering vectors of each beam, $\vec{q}_{B,G}$, are identical, as shown schematically in Figure 3.6, where indices B and G refer respectively to blue and green. Thus blue and green lasers illuminate the sample with an inter-beam angle of $2\alpha$ and detectors
measure the light scattered at the corresponding scattered propagating vectors, $\vec{k}_{B, G}^F$, separated by an angle of $2\alpha$. Then a cross-correlation of the intensities, $I_B$ and $I_G$, allows the suppression of the multiple scattering components:

$$\vec{q}_{B, G} = \vec{k}_{B, G}^F - \vec{k}_{B, G}^0$$

Eq. 3.5

$$q_{B, G} = \frac{4\pi m}{\lambda_{B, G}} \sin \left( \frac{\theta_{B, G}}{2} \right)$$

Eq. 3.6

where B and G refer respectively to blue and green, $\theta_B = \theta - 2\alpha$ and $\theta_G = \theta + 2\alpha$ are the scattering angles so that $\vec{q}_B = \vec{q}_G$.

![Scattering vector diagram](image)

Figure 3.6: Scattering vector diagram. (a) The incident $k_{B, G}^0$ and final $k_{B, G}^F$ propagation vectors of the blue and green laser beams. For every angle $\theta$, there is an angle such that the intermediate scattering vectors $q_B$ and $q_G$ are identical as shown in (b) (from [112]).

We assess the contribution of multiple scattering by comparing results from FDLS (no suppression of multiple scattering) and TCDLS in cross-correlation mode (suppression of multiple scattering). This is presented in Figure 3.7, via the normalised ISF, $f(q, \tau)$, for a relative high volume fraction at $\phi=0.519$ and three scattering vectors around the peak of $S(q)$. Both techniques agree very well and multiple scattering effects are negligible.
Figure 3.7: Comparison between FDLS (symbols) and TCDLS (cross-correlation) (lines) using XL63 for the qR values indicated. There is no contribution from multiple scattering for XL63 in the range of qR studied here.

The two ALV correlators, FDLS and TCDLS, directly give the time-average correlation function of the intensity of the scattered light:

$$g_T^{(2)}(q,\tau) = \frac{\langle I(q,0)I(q,\tau)\rangle_T}{\langle I(q)\rangle_T^2}$$

Eq. 3.7

Typically measurements are made of duration $t_{\text{run}}=1000\text{s}$, which places an upper limit in the delay time window of $\tau_{\text{max}} \sim 400\text{s}$. Should $g_T^{(2)}(q,\tau)$ decay to zero (the experimental noise floor) in this time window, then it may be reasonably inferred that this experiment of duration $t_{\text{run}}$ captures the ensemble of all intensity fluctuations. Of course the measurements are repeated to improve the statistics, particularly when decay times approach $\tau_{\text{max}}$. In such cases, the time-average is equal to the ensemble-average and $g_T^{(2)}(q,\tau) = g_E^{(2)}(q,\tau)$.

Should $g_T^{(2)}(q,\tau)$ not decay in $\sim\tau_{\text{max}}$, one could simply increase $t_{\text{run}}$. Doing so by a factor of 10 or more quickly becomes impractical if one wants to study these slowly relaxing systems under a variety of conditions.
3.2.2 Dynamic Light Scattering by Non-Ergodic Media

When the particles are partly constrained and therefore unable to explore the full ensemble of spatial configurations in the course of an experiment of reasonable duration $t_{\text{run}}$, the scattered field is no longer a zero-mean complex random Gaussian variable, and the time average is no longer equal to the ensemble average, $g_{E}^{(2)}(q,\tau) \neq g_{I}^{(2)}(q,\tau)$. Such a system is called “non-ergodic”. The Siegert relation, Eq. 2.8, cannot be applied and special procedures must be adopted to obtain the ensemble-average IACF and so obtain the ISF. However, the ergodic to non-ergodic transition is not clearly defined. As a consequence, care must be taken to identify if the sample is ergodic or non-ergodic, and then apply the corresponding techniques.

According to the state of ergodicity, different methods have been applied to probe the ensemble average IACF. To check whether or not the sample is (experimentally) ergodic or non-ergodic – i.e., there are significant fluctuations that do not relax in $\tau_{\text{max}}$ – we compare the following averages, referred as the ergodic and non-ergodic (concatenated) averages, respectively, Eq. 3.8 and 3.9:

$$g^{(E)}(q,\tau) = \frac{1}{M} \sum_{i=1}^{M} \frac{\langle I(q,0)I(q,\tau) \rangle}{\langle I(q) \rangle^{2}}$$  \hspace{1cm} \text{Eq. 3.8}

$$g^{(NE)}(q,\tau) = M \frac{\sum_{i=1}^{M} \langle I(q,0)I(q,\tau) \rangle_{i}}{\left( \sum_{i=1}^{M} \langle I(q) \rangle_{i} \right)^{2}}$$  \hspace{1cm} \text{Eq. 3.9}

where angled brackets indicate time averages. Comparison between both averaging methods is shown in Figure 3.8. From this, we infer that the first three samples ($\phi \leq 0.549$), for which $g^{(E)}(q,\tau) = g^{(NE)}(q,\tau)$, are ergodic. For $\phi = 0.555$, there are fluctuations not captured in experiments of duration $\tau = 1000s$. 
Figure 3.8: ISF as function of delay time for (lines) ergodic (Eq. 3.8) and (symbols) non-ergodic (Eq. 3.9) averaging for several volume fractions in the vicinity of the peak of $S(q)$ for XL63. Data for $\phi=0.519$, 0.540 and 0.549 were obtained from FDLS and for $\phi=0.555$ from Brute force with TCDLS.

**“Brute Force” or Discrete Sampling**

One approach is to build the ensemble-average by “brute force”, by performing a large number $M$ of measurements of the time-average IACF. This “Brute Force” (BF) method was first introduced by Pusey and van Megen in the study of colloidal glasses [115]. This method involves several independent single measurements of the time-average IACF, $g_{T,i}^{(2)}(q,\tau)$, each corresponding to a different scattering volume $V_i$ but to the same scattering vector $q$, resulting in the measurement of many independent spatial Fourier components of the density fluctuations. The motor applies a rotation of a small and arbitrary amount between measurements, controlled by a custom made Turbo Pascal program linked to the ALV-5000 software. The ensemble-average IACF is then calculating by averaging the many independent $g_{T,i}^{(2)}(q,\tau)$ using the non-ergodic or concatenated average from Eq. 3.9:

$$g_E(q,\tau) = M \left( \sum_{i=1}^{M} g_{T,i}^{(2)}(q,\tau) \langle I_i(q) \rangle_T \right) \over \left( \sum_{i=1}^{M} \langle I_i(q) \rangle_T \right) \over M \right)$$

Eq. 3.10
For \( \phi_m < \phi < \phi_c \), the sample approaches the experimental ergodic-to-non-ergodic transition and the time-average is not fully equal to the ensemble average. For samples in this range of volume fractions, we performed 200 runs of 1000s duration, to capture all fluctuations and get reasonable statistics. The duration of experiments (\( t_{\text{run}}=1000s \)) is long enough to observe the full decay of the ISF.

At \( \phi > \phi_c \), the sample is fully non-ergodic. In such cases, thousands of independent measurements are necessary to get statistically meaningful results. The ISF of a colloidal glass does not fully decay in our experimental time window (10000s). Performing thousands of experiments of 1000s duration each would be prohibitive. As a consequence, BF applied to colloidal glasses only allows the determination of the ISF at short times (\( \tau < 100s \)) and other procedures must be applied to probe the dynamics at longer times (\( \tau > 100s \)).

Moreover, this approach cannot be applied if samples are non-stationary (i.e. if they exhibit ageing) - for example for \( M=100 \) (fewer than the thousands normally needed) and \( t_{\text{run}}=1000s \), the total experiment duration is 30h and does not allow the study of the non-stationary behaviour of the sample. Thus for colloidal glasses, especially those that show ageing behaviour, an alternative method must be used.

**Pusey and van Megen method**

The Pusey & van Megen (PvM) method [115, 128] assumes that density fluctuations can be decomposed into an arrested, time invariant, component, and a fluctuating, time-dependent, component associated with local particle motions, \( \Delta \vec{r}_j(t) \), about fixed positions \( \langle \vec{r}_j \rangle \).

\[
\vec{r}_j(t) = \langle \vec{r}_j \rangle + \Delta \vec{r}_j(t)
\]

Eq. 3.11

The resulting scattered light field comprises a constant component, \( E_c(q,\tau) \), and a fluctuating component, \( E_f(q,\tau) \).

\[
E(q,\tau) = E_c(q,\tau) + E_f(q,\tau)
\]

Eq. 3.12

Then, provided the spatial correlation of both components is much smaller than the linear dimension of the scattering volume, the fluctuating field is a complex, Gaussian variable of zero mean. These considerations lead to the following expression for the ISF [115]:
\[ f(q, \tau) = 1 + \frac{\langle I(0)I(\tau) \rangle_T - \langle I^2 \rangle_T}{\langle I^2 \rangle_T + 1}^{1/2} - 1 \]  

Eq. 3.13

where \( \langle \cdot \rangle_T \) refers to the time average over the intensity fluctuations of a single speckle (or spatial Fourier component of the particle number density fluctuations) accumulated in a single measurement of duration \( t_{\text{run}} \), and \( \langle \cdot \rangle_E \) refers to the ensemble-average, acquired by averaging a large number (~4000) of speckles, achieved here in a single rotation of the sample. The non-ergodicity parameter, \( f(q, \infty) \), follows from Eq. 3.13 in the limit \( \tau \to \infty \) [128]:

\[ f(q, \infty) = 1 + \frac{\langle I \rangle_T}{\langle I \rangle_E} \left[ 2 - \left( \frac{\langle I^2 \rangle_T}{\langle I \rangle_E} \right)^2 \right]^{1/2} - 1 \]  

Eq. 3.14

Previous work confirms the validity of this method, at least for the hard-sphere colloidal glass [123]. In that the derivation of the above Eq. 3.14 assumes that the ISF decays through Gaussian density fluctuations to a constant, finite value, \( f(q, \infty) \), the dynamics are presumed to be stationary during the course of a measurement of duration \( t_{\text{run}} \). In turn this places an upper limit on the dynamic window where stationarity is, at least approximately, maintained.

For the colloidal glasses studied here, we find, by conducting measurements with a range of accumulation times \( t_{\text{run}} \), that stationarity is observed for delay times up to approximately 10s-100s. So slower decays occurring at longer times need to be measured with other methods (Echo DLS, see next section). Thus the time-average intensity \( \langle I \rangle_T \) and IACF \( g_i^{(2)}(q, \tau) \), required in Eq. 3.13, are measured for an accumulation time of 10-100s. The ensemble-average intensity \( \langle I \rangle_E \) is measured by continuously rotating the sample slowly for 10s-100s.

**Echo DLS**

The echo DLS method, developed by Pham et al., is an efficient technique for the measurement of the ensemble average IACF. Details of the technique can be found elsewhere [129]. The method consists of illuminating the particle suspension with a laser and applying a continuous rotation of the sample while measuring the intensity scattered by the sample with a detector (PMT), at a specific scattering angle \( \theta \). At a certain time \( t \), a speckle "i" illuminates the detector. At every revolution of the sample \( nT \), where \( n \) and \( T \) are respectively the number and period of the revolution, the same speckle "i" illuminates the detector. The time average IACF of the speckle "i", \( g_i^{(2)}(q, \tau) \), is calculated at every delay time \( \tau = nT \) and results in peaks,
or echoes. The maximum height of the peak corresponds to the speckle “i”. Either side of the
peaks corresponds to multiple speckles. During one rotation, thousands of speckles (~4000)
illuminate the detector and thus thousands of time average IACFs are calculated over a
measurement time scale corresponding to the last delay time of interest, typically $10^4$ s for our
colloidal glasses. Pham et al. [129] found that the shape of the peak is independent of the
samples and depends only on how many speckles are measured, and the rotation quality. For
colloidal glasses, every speckle corresponds to a sub ensemble “i” of the full ensemble of
spatial configurations. Averaging the independent IACF of all sub ensembles gives the IACF
of the full spatial configuration.

$$g_E^{(2)}(q, \tau) = \langle g_{i,j}^{(2)}(q, \tau) \rangle$$

Eq. 3.15

The brackets $\langle \rangle_i$ denote an average over ~4000 of independent speckles. Due to the
limitations of the accuracy of the rotation period, and to minimize the risk of disturbing the
particle dynamics, the period of the rotation is limited to $T=1s$ or $2s$, thus providing the lower
limit on the measured delay time. The maximum delay time is fixed by the measurement time,
typically $10^4$ s for our samples. Thus the Echo DLS method must be combined with another
technique (BF or PvM) which measures the particle dynamics at shorter delay times [46].

The advantages of the Echo technique over the Interleaved Sampling Correlator (ISC), used in
previous work [46], is that echo DLS take into account a correction for imperfect rotation. A
good quality rotation is the key to both the echo DLS and ISC techniques. An imperfect
rotation will cause a slight translation in time of the peak corresponding to the speckle “i”,
then reducing the peak height and increasing their width. However, as shown by Pham et al.
[129], the area under the peak is not affected by the rotation quality as long as the peak is
detected. Thus the area under the ensemble average peak as a function of delay time describes
the ensemble average IACF, $g_E(q, \tau)$, and is calculated as:

$$g_E^{(2)}(q, \tau) = \frac{A(nT)}{A(0)} \left[ g^{(2)}(q,0) - 1 \right] + 1$$

Eq. 3.16

Where $A(nT)$ and $A(0)$ correspond to the area under the $n^{th}$ and zero$^{th}$ peaks, and $g^{(2)}(q,0)$ is
the height of the zero$^{th}$ peak. A stepper motor is used to rotate the sample and control of the
periodicity allows a correction for the speed of the motor.

A special sample holder is used together with the motor to ensure a clear and smooth rotation
required for the Echo DLS. The sample rotation system is shown schematically in Figure 3.9.
Figure 3.9: Schematic of the sample rotation required for BF, ISC and Echo DLS. The Teflon part in contact with the cylindrical cell rotates with the cell (the bearing and second Teflon part are fixed). The conical base and blocking ring ensure no motion or vibration of the sample. The motor rotates two pins, which contact the pins attached to the sample cell cap, providing the rotation.

**Overlapping PvM & echo DLS**

Echo DLS allows the calculation of the normalised ISF, \( f(q, \tau) \), from the measured ensemble-average IACF via the Siegert relation:

\[
g_E^{(2)}(q, \tau_{\text{min}} < \tau < \tau_{\text{max}}) = 1 + c |f(q, \tau)|^2
\]

Eq. 3.17

where \( \tau_{\text{min}} \approx 1 \text{s}, \tau_{\text{max}} \approx 10^4 \text{s} \). However, \( c \) is determined by the coherence area, imperfect rotation, etc… and cannot be evaluated independently. Therefore in practice \( c \) is adjusted so that \( |f(q, \tau)|^2 \) overlaps smoothly with the PvM or BF methods. This is shown in Figure 3.10.
Figure 3.10: Overlapping between PvM method and echo DLS of (a) the ensemble-average IACF, $g_E^{(2)}(q,\tau)$, and (b) the normalised ISF, $f(q,\tau)$.

**Effects of Rotation**

We perform several experiments to check for possible artefacts on the particle dynamics (ISF) due to the rotation of the sample, as well as the reliability of the analysis applied to the ISF. First we use several different values of the duration time of an experiment and two values of the period of rotation ($t_{run}$, $T$). Figure 3.11 shows the effect of these parameters on the $t_\varphi$-dependency of $f(q,\tau)$ at two delay times, $\tau=1500s$ and $\tau=8200s$ for $\phi=0.600$. As can be seen the different measurements are in excellent agreement, showing that changing either the measurement duration or the rotation time does not affect the results. As additional criteria for these checks, we use the stretching index $\nu_c$ and delay time $\tau_m^c$, calculated from a separate series of experiments. These quantities, introduced in Chapter 2, identify the non-Fickian processes and are shown in Figure 3.12.
Figure 3.11: $t_w$-dependency of the normalised ISF, $f(q, \tau)$, at two delay times, $\tau=1500$s and $\tau=8200$s at $\phi=0.600$ and $qR=3.30$ for several values of the duration time and the period of rotation ($t_{\text{run}}$, $T$). Data shown are for XL63.

Figure 3.12: $t_w$-dependency of (a,c) the stretching index, $\nu_c(q)$, and (b,d) delay time, $\tau_m(q)$, for (left column) several duration times and two periods of rotation ($t_{\text{run}}$, $T$) at $qR=3.57$ and (right column) two different starting times of the sample rotation, $T_{\text{rot}}$, at $qR=4.15$. Data shown are from XL52.
Second, we also determine if the time for which the sample is rotated makes any difference to the ageing measurements. In a standard experiment the sample begins rotation almost immediately after tumbling ceases, and experiments are then conducted at a range of waiting times with the sample rotating continuously. In the right column of Figure 3.12, we show two experiments. One where the sample rotation starts at $t_w=30$ min ($T_{rot}=0h30$), and the second where rotation starts at $t_w=24$ hours ($T_{rot}=24h$). In all cases, the results agree very well, and it is clear that the time of the rotation does not affect the ageing dynamics.

### 3.3 Summary of Procedures

For a non-ergodic but stationary system (somewhere between $\phi_m$ and $\phi_g$), a full decay is observed during an experiment of reasonable time (~1000s) and thus the brute force technique is the most efficient to determine the ensemble average IACF for such a system. For a non-ergodic and non-stationary system ($\phi > \phi_g$), the full decay of the ISF is not observed for an experiment time of ~10000s, and thus brute force is not applicable to probe long time windows ($\tau > 100s$). For such systems, the initial or short-time decay of the ISF associated with the fast process is determined by BF and/or PvM, and the final or long-time decay of the ISF is determined by echo DLS. A custom made “Igor Pro” program was developed during this work which allowed the manipulation, analysis and calculation of thousands of files and functions. The techniques and procedures are summarised in Table 3.3 according to volume fraction.

<table>
<thead>
<tr>
<th>Volume Fraction</th>
<th>$\phi \leq 0.549$</th>
<th>$0.549 &lt; \phi \leq 0.563$</th>
<th>$\phi &gt; 0.563$</th>
</tr>
</thead>
<tbody>
<tr>
<td>State</td>
<td>Ergodic</td>
<td>Non-ergodic</td>
<td>Non-ergodic</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Stationary</td>
<td>Non-stationary</td>
</tr>
<tr>
<td>Technique</td>
<td>FDLS: $6.10^6s&lt;\tau&lt;10^3s$</td>
<td>BFTCDLS: $10^6s&lt;\tau&lt;10^3s$</td>
<td>PvM: $1\mu s&lt;\tau&lt;10^{-5}s$</td>
</tr>
<tr>
<td></td>
<td>TCDLS: $10^3s&lt;\tau&lt;10^6s$</td>
<td></td>
<td>Echo DLS: $1s&lt;\tau&lt;10^5s$</td>
</tr>
<tr>
<td>Procedure</td>
<td>50 runs $t_{run}=10^3s$</td>
<td>200 runs $t_{run}=10^3s$</td>
<td>Overlapping at 1s</td>
</tr>
</tbody>
</table>

Table 3.3: Techniques and procedures used according to volume fraction.
Chapter 4. Collective and Self dynamics

In this chapter we present DLS results for particle suspensions with volume fractions, \( \phi \), spanning from a very dilute fluid, \( \phi = 0.01 \), up to \( \phi = 0.60 \) well above the glass transition identified at \( \phi_g \sim 0.565 \) ([56, 59] and section 3.1). We assess the collective dynamics by measuring the coherent ISF’s for XL63 samples, using different experimental procedures depending on the volume fraction. For \( \phi \leq 0.549 \), samples are ergodic and stationary, and standard DLS procedures are employed using the FDLS instrument. At \( \phi = 0.555 \) and 0.563~\( \phi_g \), samples are non-ergodic but stationary, and the “Brute Force” method is carried out on the TCDLS instrument. For \( \phi > \phi_g \sim 0.565 \), samples are non-ergodic and non-stationary and ISFs are constructed by combining the PvM method with Echo DLS. For samples, which show non-stationarity (ageing behaviour), only data for fully aged samples are considered here. Ageing behaviour will be considered in detail in chapter 5. The experimental procedures for ergodic, non-ergodic/stationary and non-ergodic/non-stationary samples are detailed in chapter 3.

Previous studies have focussed on the ISF. However, there are other aspects of the dynamics, which can be better exposed by alternative representations of the data. In particular the “width” function, which is the collective equivalent of the mean square displacement, and the current-current correlation function, \( C(q, \tau) \), the collective equivalent of the VAF. The calculation of these quantities enables a direct comparison with single particle properties, and provides new insights into the collective dynamics of the system. The results are presented as functions of both \( qR \) and volume fraction. The ISFs are shown in section 4.1. The “width” function is presented in section 4.2, and the collective dynamics (coherent ISF) are compared with the single-particle motion (self ISF), obtained from previous experiments performed by van Megen et al. [46, 106]. In section 4.3, we calculate the current-current correlation function (CCCF) and compare with the velocity autocorrelation function (VAF) from previous work [33, 36].

4.1 Coherent Intermediate Scattering Function (ISF)

4.1.1 Volume fraction and \( q \) dependence

Figure 4.1 to Figure 4.3 show the ISFs, \( f(q, \tau) \), as functions of delay time \( \tau \), for volume fractions below freezing (Figure 4.1), in the coexistence region (Figure 4.2), and above the glass transition (Figure 4.3). In the main panels the delay times are scaled by \( q^2 \) and the
Brownian time, $\tau_B$. The insets show $f(q,\tau)$ scaled by $\tau_B$ only. Two interesting features emerge as volume fraction increases: (i) the loss of $q^2$ scaling; and (ii) the shape (or concavity), of $f(q,\tau)$. In order to facilitate the discussion of these results, Figure 4.4 shows the Percus-Yevick structure factors for a range of volume fractions [110], with the approximate $qR$ values used in the measurements indicated by arrows.

(i) At the lowest volume fraction studied ($\phi\sim0.01$, Figure 4.1a), the ISF, shown versus $q^2\tau$, shows no $q$ dependence, with the curves collapsing onto a single curve in the main panel − this is the well known $q^2$ scaling. At $\phi=0.213$ (Figure 4.1b), where $S(q)$ begins to shows a weak peak (Figure 4.4), the $q^2$ scaling remains almost perfect. However, upon increasing the volume fraction, the peak in $S(q)$ grows − the amplitude, sharpness and peak location increase with $\phi$ − and $f(q,\tau)$ shows a progressively stronger deviation from $q^2$ scaling. This deviation is already clearly seen at $\phi=0.421$ (Figure 4.1c) and becomes more pronounced as volume fraction increases. Some of the trends observed here have been observed previously [43, 46, 58, 130]. However, one important point, which has not been noted previously concerns the mode at $q_m$, which corresponds to density fluctuations with length scale corresponding to the inter-particle distance. This mode becomes slowest at $\phi=\phi_f$, and remains slowest at all higher volume fractions. The significance of this will be discussed later.

(ii) More interesting is the fact that the shape of $f(q,\tau)$ clearly changes with volume fraction. This is seen by the appearance of a shoulder as the volume fraction increases. At low volume fractions, eg $\phi=0.213$ (Figure 4.1b), the shape of $f(q,\tau)$ is identical at all $qR$ values − the collective dynamics show little $q$-dependency. At a volume fraction of 0.421 the shape of $f(q,\tau)$ at the lowest $qR$ value probed here, $qR\sim1.0$, starts to deviate from the shape at the other $qR$ values, with the hint of a shoulder, more obvious in the inset. At a volume fraction around the freezing point, $\phi=0.498 \sim \phi_l$ (Figure 4.2a), a shoulder is now clearly observed at the lowest $qR$ value ($qR\sim1.0$) with similar behaviour emerging for the next lowest $qR$ values (1.4 and 1.8). At $\phi=0.540$, shoulders are clearly observed in $f(q,\tau)$ at lower and higher $qR$ values, respectively $qR\leq2.7$ and $qR\geq4.1$, and there is the hint of a shoulder at the $qR$ values in the vicinity of the peak of $S(q)$ ($qR=3.1, 3.5, 3.8$ and 4.1). At $\phi=0.555$, still below the glass point, $f(q,\tau)$ shows a clear shoulder at all $qR$ values, though this is less exposed in the vicinity of the peak of $S(q)$. Finally at $\phi=0.584$ and $0.600 > \phi_g$ (Figure 4.3), the ISFs at all $qR$ values from 1.9 to 3.8 have shoulders, which have become plateaus.
Figure 4.1: Coherent ISFs as functions of delay time, scaled by $q^2$ and the Brownian time $\tau_B$, for the qR values indicated, for volume fractions below freezing: (a) $\sim 0.01$; (b) 0.213; and (c) 0.421. The insets show the same data not scaled by $q^2$. 
Figure 4.2: Coherent ISFs as in Figure 4.1, for volume fractions between freezing and the glass transition: (a) 0.498; (b) 0.540; and (c) 0.555.
Figure 4.3: Coherent ISFs as in Figure 4.1, for volume fractions above the glass transition: (a) 0.584 and (b) 0.600.
Figure 4.4: Percus-Yevick prediction of the structure factor $S(q)$ for polydispersity of 8% as a function of $qR$ at the volume fractions indicated [110]. The arrows indicate approximately the values of $qR$ probed in the experiments.

4.1.2 Volume fraction dependence at $q_m$

Figure 4.5 shows $f(q,\tau)$ for volume fractions spanning from dilute ($\phi\sim0.01$) up to the glass region ($\phi=0.600$) in the vicinity of the peak of $S(q)$, at $qR=3.5\sim q_mR$. A change in the dynamics of ~6 orders of magnitude is observed between the dilute sample and the glassy samples. The ISF for a dilute sample decays exponentially with delay time. This exponential decay, represented as a dashed line in Figure 4.5 is associated with a free particle diffusive process, also called a Markovian or Fickian process (no interparticle interactions). As the volume fraction increases, $f(q,\tau)$ deviates from an exponential decay and can be fit (approximately) to a stretched exponential function, also called the Kohlrausch function, up to $\phi=0.498$, implying that the dynamics may be described by a distribution of diffusive processes. These fits are shown as solid lines in Figure 4.5. For $\phi > 0.498$, deviations from the Kohlrausch function emerge, and for $\phi > 0.540$ $f(q,\tau)$ the data can no longer be described by such a function, suggesting that some non-diffusive process contributes to the decay. Moreover, for $qR$ values away from the peak, the deviations from the Kohlrausch function occur at lower volume fraction. For example at $qR\sim1.0$, the deviation appears at $\phi\sim0.421$. 
These results show an increasing complexity of the structural rearrangements as the volume fraction is increased.

Figure 4.5: Coherent ISFs as in Figure 4.1, for all measured volume fractions at qR=3.5, in the vicinity of the peak of the structure factor (q~q_m). Lines and dashed line are respectively stretched exponential fits and exponential fits to the data. The data shown in black (\( \phi \geq 0.563 \)) are from fully aged samples at qR=3.30 obtained from combination of PvM method and echo DLS (see chapter 5).

### 4.2 Fickian and non-Fickian processes: the Width function.

One way to analyse the data is to calculate the “width” function \( w(q, \tau) \) from the coherent ISF by analogy with the Mean-Square Displacement (MSD) from the self-ISF. Without loss of generality the ISF can be written as,

\[
f(q, \tau) = \exp[-q^2 w(q, \tau)].
\]

Eq. 4.1

Like the MSD, the width function of a dilute sample grows linearly with the delay time in its full time window. In addition it has no q-dependency, as \( S(q)=1 \). This means that density fluctuations on all wavelengths relax by the same mechanism, namely, free particle diffusion. However, at higher volume fractions this is not the case, and the width function exposes deviations from free-particle diffusion by the identification of non-linear behaviour in a specific time window.
As the volume fraction increases, a separation (a plateau) between short-time and long-time diffusive regimes becomes apparent. Where separate short-time and long-time diffusive behaviour is observed, an inflection point between the two can be unambiguously identified. This inflection point, the point of maximum stretching of the width function, characterises the crossover between a fast (short-time) process associated with local diffusion motions (or diffusion of the particles within their neighbour cages) and a slow (long-time) process, associated with diffusion over larger distances.

The short-time processes are characterized in section 4.2.1. The inflection point will be presented in section 4.2.2. The long-time behaviour will be discussed in section 4.2.3. In section 4.2.4, the collective dynamics measured here are compared with single particle dynamics measured previously. This is used to express the collective dynamics in terms of single-particle motion, which is presented in section 4.2.5.

4.2.1 Short-time collective dynamics

The width function \( w(q,\tau) \) is shown in Figure 4.6 and Figure 4.7, for several volume fractions and \( qR \) values. The diffusive short-time dynamics, where \( w(q,\tau) \) grows in proportion to delay time, \( \tau \), are commonly considered [116] and characterised by a short-time diffusion coefficient \( D'_s(q) \). One way to calculate \( D'_s(q) \) is to apply a linear fit using Eq. 4.2, over the delay time range where \( w(q,\tau) \) grows linearly.

\[
\log(w(q,\tau)) = \log(D'_s(q)) + \log(\tau)
\]

Eq. 4.2

For illustrative purposes, such fits are shown in Figure 4.6 and Figure 4.7 for \( q_mR \). Figure 4.8 shows the ratio \( D_o/D'_s(q) \) at several volume fraction, where \( D_o = 435 \text{ nm}^2\text{ms}^{-1} \) (at T=30°C) is the free-particle or Stokes-Einstein diffusion coefficient. As defined in Eq. 2.18, \( D_o/D'_s(q) \) scales approximately with the structure factor \( S(q) \) (Figure 4.4). This result is consistent with previous studies by Segre et al. [111] and van Megen et al. [131]. In the dilute limit, where \( S(q)=1 \), \( D_o/D'_s(q) \) has no \( q \)-dependency and \( D'_s(q) = D_o \). As the volume fraction increases, a peak forms in \( D_o/D'_s(q) \), as it does for \( S(q) \). This implies that the short-time dynamics are slowest at \( q_m \) – this is the well-known de-Gennes narrowing [116].

While the low-\( q \) dependency of \( D_o/D'_s(q) \) follows approximately \( S(q) \), the high \( q \)-dependency deviates strongly from \( S(q) \) scaling – \( S(q) \) decreases at high \( q \) with \( \phi \) (see Figure
4.4), which contrasts with the behaviour of $D_s/D_i(q)$. These deviations from $S(q)$ scaling, most pronounced at high $q$, are due to hydrodynamic interactions [132].

Figure 4.6: The width function, $w(q,\tau)$ in nm$^2$, as a function of delay time at qR values indicated for volume fractions below and at freezing: (a) $\phi=0.213$, (b) $\phi=0.421$ and (c) $\phi=0.498-\phi_f$. Lines are linear fits of slope one at short time (solid lines) and long time (dotted lines) at $\sim qm$. 

\[ w(q,\tau) \]
Figure 4.7: The width function, $w(q, \tau)$ in nm$^2$, as a function of delay time at qR values indicated for volume fractions around melting and above the glass transition: (a) $\phi=0.540 < \phi_m$, (b) $\phi=0.555 > \phi_m$ and (c) $\phi=0.584 > \phi_g$. Lines are linear fit of slope one at the short time (full lines) and long time (dotted lines) at $\sim q_m$. 
Figure 4.8: $D_0/D_s(q)$ as function of $qR$ at several volume fractions. $D_s(q)$ is calculated by a line fit of Eq. 4.2 in the short-time limit.

**4.2.2 Collective dynamics at the inflection point**

The inflection point – the crossover between the fast and slow processes – is identified as the point where the maximum deviation from diffusive behaviour occurs. Thus this point can be used to quantify the non-Fickian processes participating in the dynamics. The inflection point is determined by finding the minimum in the logarithmic derivative of the width function defined as:

$$n(q, \tau) = \frac{d \log[w(q, \tau)]}{d \log \tau} \quad \text{Eq. 4.3}$$

$n(q, \tau)$ is represented for several volume fractions in the vicinity of the peak of $S(q)$ in Figure 4.9. A minimum in $n(q, \tau)$ is clearly observed for $\phi > 0.421$. We expose the non-Fickian, many-body aspects of the density fluctuations by focussing on this minimum, where $w(q, \tau)$ exhibits its maximum deviation from Fickian behaviour. The deviations are given by the stretching index $\nu_s(q)$:

$$\nu_s(q) = \min[n(q, \tau)]. \quad \text{Eq. 4.4}$$
For easier interpretation, the analysis will focus around the complement of the stretching index, \( c_c(q) \), which we call the non-Fickian index:

\[
c_c(q) = 1 - c_c(q).
\]

Eq. 4.5

Note that this analysis can only be carried out when a clear minimum is observed. This is not the case for lower volume fractions or qR values. Where no clear minimum is observed, the upper time limit of \( n(q, \tau) \) is taken (\( \phi < 0.421 \)).

Figure 4.9: Logarithmic derivative of the width function, \( n(q, \tau) \), as a function of delay time, scaled by \( \tau_B \), for volume fractions as indicated, in the vicinity of the peak of the structure factor (q~q_m).

This analysis provides three quantities that characterise the non-Fickian dynamics: (i) the plateau height factor \( f_c(q, \tau_m^c) \); (ii) the delay time \( \tau_m^c(q) \) where maximum stretching occurs; and (iii) the non-Fickian index \( c_c(q) \). Figure 4.10 shows a schematic of the width function and ISF versus delay time and highlights the dynamical quantities measured and required for the rest of the analysis.

The q-dependency of the plateau height \( f_c(q, \tau_m^c) \) is presented in Figure 4.11 at several volume fractions. \( f_c(q, \tau_m^c) \) shows a maximum at around the structure factor maximum, and
increases as the volume fraction is increased. The plateau height factor $f_c(q, \tau_m^c)$ quantifies the fraction of particles that are caged – as expected the fraction of the “caged” particles increases with the volume fraction.

Figure 4.10: Schematic diagram showing the dynamical quantities measured.

Figure 4.11: Plateau height factor $f_c(q, \tau_m^c)$ as function of qR for a range of volume fractions. $f_c(q, \tau_m^c)$ shows a strong q-dependency and follows approximately $S(q)$. Lines are only to guide the eye.
Figure 4.12 shows $c_c(q)$ and $\tau_m^c(q)$, respectively, as functions of $qR$ for several volume fractions. The non-Fickian index, $c_c(q)$, expresses, on a scale from zero to one, the effect of caging. Alternatively, $c_c(q)$ can be read as the correlation of forward and backward displacements, incurred by caging, in delay time $\tau_m^c(q)$. So, for a suspension in the limit of infinite dilution, where all particles engage in random Markovian excursions, $c_c(q) = 0$, and the delay time $\tau_m^c(q)$ is undefined. For the perfect glass, where all particles are caged, $c_c(q) = 1$, and $\tau_m^c(q)$ is infinite. Outside these idealizations $\tau_m^c(q)$ is the delay time that must be exceeded for number density fluctuations of spatial frequency $q$ to forget the effects of caging. So, increasing $\tau$ beyond $\tau_m^c(q)$ results in an approach to the (long time) diffusive limit.

The variation with $q$ of both $c_c(q)$ and $\tau_m^c(q)$ decreases with increasing $\phi$. Though $c_c(q)$ retains some $q$-dependence at high volume fractions, $\tau_m^c(q)$ shows no systematic variation with $q$ at $\phi$. Of course, given the stretching of $w(q, \tau)$ at the elevated volume fractions considered here, there is more uncertainty in $\tau_m^c(q)$ than in $c_c(q)$. The data in figures 4.11 and 4.12 show that, as expected, density fluctuations become slower, and caging more pronounced, as $\phi$ increases. Where they can be discerned, minima in $c_c(q)$ and $\tau_m^c(q)$ indicate that non-Fickian processes are least subject to caging and fastest around $q_m$. This is in contrast to the behaviour of the short-time diffusive dynamics, which are known to be slowest at $q_m$ (see Figure 4.8). The minima in $\tau_m^c(q)$ at $q_m$ suggest that structural relaxation (“caging and escape of the cage”) will first occur at a local level: for individual particles. The fact that $\tau_m^c(q)$ increases at low $q$ reflects the fact that it takes longer for groups of particles to escape their cage environment. The minima in $c_c(q)$ at $q_m$ suggest that the “strength of the cage” is lower for individual particles than for groups of particles. It is easier for one particle to escape the cage than a group of particles to escape its respective cage. Moreover, we show in section 4.2.3 that the diffusive regime is not observed at low $q$ and so groups of particles cannot travel together over any significant distance, and so remain trapped in their collective “cage”, even if individual particles escape.
Figure 4.12: (top) Complement of the stretching index, $c_c(q)$, and (bottom) delay time, $\tau_m(q)$, at the crossover between fast and slow processes, scaled by the Brownian time, as functions of qR at the volume fractions indicated. At 0.421, a clear minimum of $n(q,\tau)$ is only observed around the peak. At volume fractions lower than 0.421, difficulties are encountered in defining a clear minimum, and the upper time limit is taken as an approximation.

Within the errors, for a given q one sees that both $\tau_m(q)$ and $c_c(q)$ increase with volume fraction. This trend is shown more clearly for $c_c(q)$ in Figure 4.13, where $c_c(q)$ is plotted vs.
volume fraction for several q vectors. Around the structure factor peak the data appear to overlap for all volume fractions.

![Graph](image.png)

**Figure 4.13:** Collective and self non-Fickian indices, $c_c(q)$ and $c_s$, (see section 4.2.4), as functions of volume fraction at qR values indicated.

We observe a change in the behaviour between low and high $\phi$. To quantify this, the data are re-graphed on a log-log scale in Figure 4.14. Figure 4.14a shows the data at qR=3.5, and the lines corresponds to line fits $\log(c_c(\phi)) = a + b\log(\phi)$ at low $\phi$ and high $\phi$ ranges. The change in slope occurs at a “crossover” volume fraction, determined from these fits to be $\phi_c=0.495$, which coincides with the freezing volume fraction $\phi_f$ (indicated by the vertical dashed line). Of course there is always some ambiguity in deciding which data range to choose for each fit. In order to test if the crossover is robust, a linear regression analysis was conducted for both low and high $\phi$ ranges. Using different ranges of data (eg using data points labelled A1-A4, A1-A5 etc in Figure 4.14a), we can determine the data range which maximizes Pearson’s coefficient ($R^2$) and minimizes the relative errors in a and b, respectively $\Delta/a$ and $\Delta/b$ (see Table 4.1). By taking the optimum fits at low and high $\phi$, respectively A1-A7 and B1-B6, the intersection gives a critical volume fraction of 0.495-\phi_c. Using the values either side of this (eg. A1-A6 and B1-B5) and calculating the intersection yields an error of 0.001.
Figure 4.14: Non-Fickian index, $c_s(q)$, on a log-log scale for qR values of (a) 3.5 and (b) 2.7 and 3.8 in both side of the peak of $S(q)$. Lines are short time and long time fits. The intersection between the fits is at $\phi = 0.495 \pm 0.001$ ($\sim \phi_f$). Extrapolation to $c_s(q) = 1$ is at $\phi = 0.569 \pm 0.001$. 


Table 4.1: Values of the line fit parameters, a and b, of log($c_c(\phi)$) = a + b log($\phi$) as function of volume fraction for (a) low $\phi$ and (b) high $\phi$, for qR=3.5.

This analysis is convincing at qR=3.5, but does it also hold true for other q around the peak? Figure 4.14b shows the results of a similar analysis for two other qR values. In both cases the overlap is at $\phi_c$=0.495. Moreover, it appears that this change in dynamics also holds at lower q, but occurs at a higher volume fraction, e.g. $\phi$~0.53 for qR=1.0.

As a conclusion, this is strong evidence that there is a qualitative change in the dynamics near the structure factor peak at $\phi_c$. This change is a signature of the non-Fickian processes responsible for the dynamics in the metastable fluid above $\phi_c$. Another interesting point is that the extrapolation of the high volume fraction fit to $c_c(q)$=1, ie representative of a fully arrested system, occurs at $\phi$=0.569±0.001 (at qR=2.7, 3.5 and 3.8). This value is very similar to previous experimental observations of the glass transition point – $\phi_g$~0.565-0.57 ([56, 59] and section 3.1).

4.2.3 Long-time collective dynamics

By analogy with the short-time diffusion coefficient, a long-time diffusion coefficient is commonly defined where $w(q, \tau)$ grows linearly with delay time in the long-time range $\tau >> \tau_m(q)$. It is obvious from Figure 4.6 and Figure 4.7 that difficulties occur in identifying linear long-time behaviour at some q values. As mentioned previously, $f(q, \tau)$ and $w(q, \tau)$ attain the experimental noise floor before the anticipated long-time diffusion is observed. A long-time diffusive behaviour can be discerned at $q_m$ for $\phi \geq 0.498$ but this is not the case at
other q values. Moreover, on approaching \( \phi_g \), the long-time diffusive behaviour expands to longer times and our time window only shows a hint of diffusive behaviour. Alternatively, both short and long-time diffusion coefficients can be determined by calculating the time-dependent diffusion coefficient \( D(q, \tau) \), defined as [111]:

\[
D(q, \tau) = -\frac{1}{q^2} \frac{d \ln f(q, \tau)}{d \tau}
\]

Eq. 4.6

For illustrative purpose, we show, in Figure 4.15, \( D(q, \tau) \) as function of delay time for several volume fractions in the vicinity of the peak of \( S(q) \). The short-time, \( D_s(q) \), and long-time, \( D_l(q) \), diffusion coefficient are identified by plateaus where \( D(q, \tau) \) is a constant [116]. Clear plateaus are observed at short-times, justifying the existence of \( D_s(q) \) at all qR. The diffusion coefficients thus determined are in agreement with the values determined directly from the width function.

It is a more complex task at long-times, where plateaus are not clearly observed except at \( q_{m} \). The \( \phi \)-dependency of \( D_l(q_m) \) is shown in Figure 4.16 and decreases monotonically as \( \phi \) increases. This will be discussed below.

![Figure 4.15: Time-dependent collective diffusion coefficient, \( D_c(q, \tau) \), as a function of delay time for several volume fractions at \( q \approx q_{m} \), in the vicinity of the peak of \( S(q) \).](image)

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4.2.4 Comparison of collective and self dynamics.

Since we have at our disposal previous measurements of the self-ISF [46, 106], we can compare the particle number density fluctuations (or collective dynamics) with the single particle motion (or self dynamics). By analogy with section 4.2.1, 4.2.2 and 4.2.3, we can define the following quantities: self-short and long-time diffusion coefficients, $D_s^s$ and $D_l^s$, respectively, where the MSD grows linearly with delay time; a self non-Fickian index, $c_s$, corresponding to the slope of the MSD at the crossover between fast and slow processes; and a self delay time, $\tau_m^s$, at the crossover.

For illustrative purposes we show, in Figure 4.17, the MSD and the “width” function at $\sim q_m$ for the volume fraction, $\phi = 0.531$, about midway between the first order and glass transition values. The dashed lines are the fits defining short and long time diffusive regimes. The arrows define the crossover between fast and slow processes. We compare: (i) $c_c(q_m)$ with $c_s$ shown in Figure 4.18 (top), (ii) $\tau_m^c(q_m)$ and $\tau_m^s$, shown in Figure 4.18 (bottom), and (iii) $D_l^c(q)$ and $D_l^s$ shown in Figure 4.16.
(i) From Figure 4.18a, we observe that \( c_s \) converges to \( c_s(q_m) \) as \( \phi \) approaches \( \phi_g \) but differs significantly at \( \phi < \phi_g \) (note the log scale).

(ii) Figure 4.18 (bottom) shows that, within experimental error, \( \tau_m^c \) coincides with the minimum value of \( \tau_m^c(q_m) \) for \( \phi \geq 0.421 \).

(iii) Figure 4.16 shows that \( D_l^c(q_m) \) and \( D_l^l(q_m) \) are completely consistent but \( D_l^c(q_m) > D_l^l(q_m) \).

Figure 4.17: MSD, \( \langle \Delta r^2(\tau) \rangle / 6 \) (circles), and the width function, \( w(q_m, \tau) \) (squares), versus delay time \( \tau \) at \( \phi \sim 0.53 \). Dashed and filled arrows indicate respectively times \( \tau_m^c \) and \( \tau_m^l(q_m) \). Distances are expressed in units of the particle radius and times in units of the Brownian time \( (\tau_B = R^2/6D_o) \). Dashed lines of unit slope indicate diffusive limits.
Figure 4.18: (top) $c_c(q_m)$ (squares) and $c_s$ (circles), (bottom) $\tau_c^c(q_m)$ (squares) and $\tau_m^s$ (circles) as functions of volume fraction.

4.2.5 Collective dynamics in terms of single-particle motion.

From the data in [46, 106], we obtain also the MSD for each volume fraction that matches as closely as possible that of measurements of the coherent ISF. Then for each value of $\tau_m^c(q)$, where the coherent ISF has its maximum stretching, we read the MSD, $\langle \Delta r^2(\tau_m^c(q)) \rangle$, at that delay time. This quantity, shown in Figure 4.19, represents the mean-squared distance particles must traverse in order for number density fluctuations of wavevector $q$ to lose memory of the effects of caging. To avoid the possibility of confusion in this unconventional analysis, we emphasize that the $q$-dependence of the MSD, $\langle \Delta r^2(\tau_m^c(q)) \rangle$, enters implicitly
through the q-dependence of the delay time $\tau_m^c(q)$. That these MSDs, $\langle \Delta r^2(\tau_m^c(q)) \rangle \approx 0.15$, are smallest at $q_m$ is consistent with the q-dependence of $\tau_m^c(q)$ see in Figure 4.12b. As also anticipated from the behaviour of $\tau_m^c(q)$, but striking nonetheless, $\langle \Delta r^2(\tau_m^c(q)) \rangle$ loses its q-dependence with increasing $\phi$.

As shown in previous work [36, 37] and in Figure 4.19 (inset), as $\tau_m^c(q_m) = \tau_m^i$, the value of the MSD at the delay time, $\tau_m^i$, of its maximum stretching shows essentially no systematic variation at volume fractions higher than $\phi_f$. Since $\tau_m^c(q_m) = \tau_m^i$, as seen in Figure 4.18 (bottom), $\langle \Delta r^2(\tau_m^i(q)) \rangle (-0.15)$ displays the same lack of sensitivity to the volume fraction. This saturation of the MSD hints at an interruption in the decay of density fluctuations of spatial frequency $q_m$ due, presumably, to some structural impediment. As far as we can gauge, from the stretching of the ISFs, this interruption, or pause, sets in around the freezing volume fraction, $\phi_f$ (see fig.4 of [36]). Then as $\phi$ increases it is seen to spread to other wavevectors from $q_m$ in both directions. In particular, large-scale displacements, generally exposed at lower $q$, decrease most as $\phi$ approaches $\phi_g$. It appears that at $\phi_g$ number density fluctuations, at least within the measured range of spatial frequencies, $1<qR<5$, all pause at the same MSD, $\langle \Delta r^2(\tau_m^i(q)) \rangle \approx 0.15$.

As mentioned in section 4.2.3, the identification of a long-time diffusive regime for the collective dynamics (coherent width function) is clearly observed around $q_m$ but rather questionable away from $q_m$. So the following question can be asked: does a long-time diffusive regime exist for all $q$? We consider the quantity $\langle \Delta r^2(\tau_m^c(q)) \rangle$, which corresponds to the distance a particle has to move for the number density fluctuations to forget excluded volume effects. One sees, from Figure 4.19, that at $\phi_f$ $\langle \Delta r^2(\tau_m^c(q_m)) \rangle$ is smaller by a factor of $\approx 5$ compared to $\langle \Delta r^2(\tau_m^c(q)) \rangle$ at $qR=1.0$. This quantifies the difficulty in identifying the long-time diffusive behaviour from the coherent ISF at q vectors away from the peak of the structure factor, simply because particles are unable to move the distances necessary for the number density fluctuations to forget packing constraint effects.
Figure 4.19: MSDs at delay times $\tau_m(q)$ versus qR for volume fractions indicated. For clarity not all volume fractions are included in the main panel. Inset shows $\langle \Delta r^2(\tau_m(q)) \rangle$ at qR=1.5 (circles), qR=3.5 ($\sim q_m R$) (filled diamonds), qR=4.5 (squares), and $\langle \Delta r^2(\tau) \rangle$ (filled diamonds) as functions of volume fraction.

### 4.3 Current-Current Correlation Function (CCCF)

In this section we present experimental determinations of the current-current correlation function (CCCF), introduced in section 2.4.3. We first present the results of the short-time behaviour of the CCCF, then we focus on the long-time tail of the CCCF by plotting its absolute value and finally we compare the CCCF with the VAF.

Figure 4.20 show the CCCF, $C(q,\tau)$, as functions of the delay time for several q values and volume fractions. First, over most of the accessible time window all CCCFs are negative and monotonically approach zero from below. Whether or not $C(q,\tau)$ is positive or negative at very short-times is unclear from these data – in some cases, there appears to be a minimum in $C(q,\tau)$, this is not always observed due to the noise. However assuming that the fastest detectable process is diffusion, as characterised by $D^r_c(q)$, i.e.:

$$f(q,\tau \to 0) = \exp[-q^2D^r_c(q)\tau]$$

Eq. 4.7
Then the CCCF in the zero time-limit becomes:

$$C(q, \tau \to 0) = -q^4 D_s^{1/2}(q) \exp[-q^2 D_s^{1/2}(q) \tau].$$  \hspace{1cm} \text{Eq. 4.8}

In other words, the amplitude of the CCCF should scale as $q^4 D_s^{1/2}(q)$. A strong q-dependency of $C(q, \tau)$ is found at low volume fraction but seems to decrease as $\phi$ increases. Whether or not the q-dependency vanishes at $\phi_g$ is not clear from this representation.

Figure 4.20: CCCF, $C(q, \tau)$ in ms^-2, at several qR values for (a) $\phi=0.213$, (b) $\phi=0.540$ and (c) $\phi=0.584$. Note that CCCF is negative and short-time amplitude decreases as volume fraction increases.
In order to expose the long-time tail of the CCCF, we plot the absolute value of the CCCF, \(|C(q,\tau)|\), for several volume fractions and q values in Figure 4.21, Figure 4.22 and Figure 4.23. The insets show the normalised CCCF, \(C(q,\tau)/C_0(q)\), as functions of \(q^2 \tau/\tau_B\), where \(C_0(q)\) corresponds to the zero-time limit assuming a diffusion process:

\[
C_0(q) = -q^4 D_{\text{eff}}^2(q) 
\]

Eq. 4.9

At low volume fraction (\(\phi=0.213\)), \(|C(q,\tau)|\) shows a q-dependency consistent with the expected scaling at all \(\tau\).

Two important features appear in \(|C(q,\tau)|\) as \(\phi\) is increased. First, the q-dependency of \(|C(q,\tau)|\) decreases. At \(\phi \geq 0.563-\phi_g\), for all qR probed (from 1.2 to 5.3), the data follow a master curve, exposing a q-independency or scale invariance of \(|C(q,\tau)|\). Second, in the vicinity of the peak of \(S(q)\), a power law decay emerges at \(\phi \sim 0.498-\phi_f\), with a slope of -3/2, as seen in Figure 4.24. This power law behaviour becomes clearer as the volume fraction increases and become very strong in the glass (Figure 4.23). This behaviour is highlighted in Figure 4.24, where the CCCFs are plotted for all volume fractions at \(q_m\), with each curve offset for clarity. Lines are power law fits to the data in a specific time range. Figure 4.25 shows the exponent or slope of the power law fits as a function of volume fraction. As \(\phi\) increases, the slope of the power law decays of \(|C(q,\tau)|\) decreases progressively until reaching approximately -2.4 ± 0.1 at \(\sim \phi_g\).
Figure 4.21: Absolute CCCF, $|C(q, \tau)|$ in ms$^{-2}$, as function of $\tau/\tau_B$ at several qR values for (a) $\phi=0.213$, (b) $\phi=0.421$ and (c) $\phi=0.498$. Note that a plateau appears first at $q_m$ for $\phi=0.498 \sim \phi_f$. Line is a power law fit to the data in the plateau region. Insets shows CCCF normalised by its zero time limit $C_0(q)$, calculated by cumulant expansion.
Figure 4.22: Absolute CCCF, \(|C(q,\tau)|\) in ms\(^2\), at several \(qR\) values for (a) \(\phi=0.540\), (b) \(\phi=0.555\) and (c) \(\phi=0.563\). Lines are power law fit of slope indicated. Insets shows CCCF normalised by its zero time limit \(C_0(q)\).
Figure 4.23: Absolute CCF, $|C(q, \tau)|$ in ms$^{-2}$, at several qR values for volume fraction above the glass transition: (a) $\phi=0.584$, (b) $\phi=0.600$. Lines are power law fits of slope indicated.

Previous work [33, 36] focused on the measurement of the VAF. In that work it was also been found that a power law decay of the long-time tail of the VAF emerges at $\phi_c$. The values of the exponent of the power law fit of the absolute VAF are also presented in Figure 4.25. Note that the data obtained from collective dynamics show much less noise, however the $\phi$-dependency of both exponents are consistent. At $\phi\sim\phi_c$, both are approximately equal to -1.5. However at $\phi\sim\phi_g$, exponents are -2.0 and -2.4, respectively for the VAF and the CCF. Nonetheless both show a tendency to saturate at $\phi\sim\phi_g$. Interestingly, molecular dynamics simulation of the VAF shows a power law behaviour with a slope of -5/2.
Figure 4.24: logarithm of absolute CCCF as a function of logarithmic $\tau/\tau_B$ for several $\phi$ at $q \sim q_m$. Lines are power law fits to the data. Data are offset vertically by an increment 1 as $\phi$ increases.

Figure 4.25: Slope of power law decays of the absolute CCCF (circles) (at $q_m$) and VAF (squares) as function of volume fraction. Line is a guide for the eye. The power law fits were applied in a specific time range of at least two decades. Error bars correspond to fits of different time ranges within these two decades, specific for each volume fraction.
4.4 Summary

The present results are consistent with previous work [58] as shown for example in Figure 4.1 to Figure 4.3, where there is a slowing of the dynamics as $\phi$ is increased until apparent dynamical arrest is observed above $\phi_g$. However, experimental improvements have allowed much more accurate measurements of the coherent ISF deep in the glass region, leading to new results. These new results can be summarised by two main features: the change in dynamics at $\phi_f$; and scale invariance (or saturation) at $\phi_g$.

A change in the dynamics at $\phi_f$ is observed in several ways: (i) a separation of mode $q_m$ in the ISF (Figure 4.1); (ii) deviation of the ISF from a stretched exponential; (iii) a change in the slope of the $\phi$-dependency of the non-Fickian index, $c_c(q)$ (most exposed around $q_m$ (Figure 4.14)); (iv) saturation of the $\phi$-dependency of the mean-squared displacement at maximum stretching of the width function $\langle \Delta r^2(\tau_m(q)) \rangle = 0.15$ (at $q_m$ only) (Figure 4.19); and (v) the emergence of a power law decay in the CCCF at $q_m$ with slope $\sim -1.5$.

These results reinforce previous observations of a change of dynamics at $\phi_f$: (i) the emergence of a negative algebraic decay in the VAF with slope $\sim -1.5$ from both experiment and MCT [33, 36, 37]; (ii) the emergence of non-monotonicity in the non-gaussian parameter from MCT [37]; and (iii) the disappearance, from the dynamical window, of the positive $\tau^{-3/2}$ hydrodynamic power law in the VAF, and the emergence of a negative $-\tau^{-5/2}$ power law, as observed in molecular dynamics simulations of Newtonian hard spheres [34].

A scale invariance or saturation appears in the collective dynamics at $\phi_g$. This scale invariance, suggested by the loss of significant dependence on wavevector $q$, is observed in several quantities: (i) the non-Fickian index $c_c(q)$ (Figure 4.12a); (ii) the delay time $\tau_m(q)$, at the crossover between fast and slow processes (Figure 4.12b); and (iii) the CCCF, which exhibits a negative algebraic decay with exponent $\sim -2.4 \pm 0.1$ (Figure 4.23). This scale invariance suggests that dynamics decouple from the structure, at least for those aspects of the structure probed by wavevectors in the present spatial window $1 < qR < 5$. 
4.5 Interpretation

The dynamical changes occurring at $\phi_f$ expose both qualitative and quantitative differences between the thermodynamically stable ($\phi < \phi_f$) and metastable ($\phi_f < \phi < \phi_g$) hard sphere systems. These differences clearly indicate the emergence of processes at $\phi_f$ which are characteristic of the metastable state.

Such processes are also the cause of the negative algebraic decay in the VAF and CCCF. As found by Williams et al. [34], these indicate an incompatibility with the Alder’s classical (positive) $\tau^{-3/2}$ hydrodynamic “tail”, which manifests the response to diffusing transverse momentum currents [38]. This incompatibility, as explained in detail in [36], indicates a (local) violation of momentum conservation, and an inability of the system to respond to diffusing momentum currents, i.e. viscous flow. In other words, the motion of some particles are so constrained that they are unable to respond to diffusive shear modes in the suspending liquid. So some particles are trapped in clusters, immersed in a relatively more mobile environment. This picture, known as dynamical heterogeneity, has been exposed in microscopic experiments through confocal microscopy [14-16] and numerical simulations [9, 10, 133-135]. The results of the present work confirm that these processes become manifest at the first order transition.

These structural impediments, associated with dynamical heterogeneity, start at $\phi_f$ for spatial frequencies ($q_m$) corresponding to the interparticle distance. As the volume fraction is increased, these structural impediments spread to other spatial frequencies, and the number of spatial modes by which the system can respond to diffusing momentum currents decreases. In other words, the resistance to flow increases due to a decrease in the number of spatial modes by which the system can respond to diffusing momentum currents. Although, for a given volume fraction in the metastable fluid, the system cannot respond to diffusing momentum currents through the spatial mode in the range $q_m \pm \delta q$, it can still to do so through those spatial modes outside this range. So the final decay ($\tau > \tau_m(q)$) of density fluctuations in this range of spatial modes, that no longer couple directly to the diffusing momentum, is delayed by the decay of those that do. So, conversely to the mechanism, proposed by Geszti [136], by which the suspension’s (relative) viscosity controls structural relaxation, the impediment to structural relaxation exposed here controls the viscosity. The coupling between flow and structural relaxation is maintained, whatever the mechanism. Accordingly, one anticipates the divergence in the delay times $\tau_m(q)$ and $\tau_m^s$, apparent from Figure 4.12b as $\phi$ approaches $\phi_g$. 

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to be accompanied by a corresponding divergence in the resistance to flow. So, although the suspension still flows, the presence of these structural impediments prevents the (Newtonian) viscosity in the limit of zero shear rate from being attained. This inference is consistent with previous work based on the VAF [33], as well as measurements of the rheology [137] of hard-sphere suspensions.

At $\phi_g$, structural relaxation becomes arrested for all spatial frequencies in the range $1 < qR < 5$ i.e. $\left\langle \Delta r^2(\tau_\varepsilon(q)) \right\rangle = 0.15$ for all $q$, so there is no spatial mode left for the system to respond to diffusing momentum currents, i.e. flow is arrested. The complete arrest of flow would indicate the transition to an ideal glass - a sharp ergodic to non-ergodic transition as predicted by the idealized MCT – kinetically observed through the apparent divergence of $\tau^*_m$ and $\tau^*_m(q)$ (Figure 4.12). Although MCT theory and experiments show good agreement [37], there is no allowance for the fact that colloidal glasses age. This will be addressed in chapter 5.

Finally, at $\phi_g$, the decay of number density fluctuations of spatial frequencies in the range, $1<qR<5$, all demand, or are effected through, root-mean squared displacements (RMSD) of the same magnitude, $R_g = \left\langle \Delta r^2(\tau_\varepsilon(q)) \right\rangle^{1/2} = \left\langle \Delta r^2(\tau_\varepsilon) \right\rangle^{1/2} = 0.36$. The corresponding value in a colloidal crystal at approximately the same volume fraction ($0.57$) is $R_x = 0.18$ [138]. The fact that $R_g$ is greater than $R_x$ by a factor of two is incompatible with the simple cage picture – the notion of a homogeneous distribution of particles in identically fluctuating neighbour cages – commonly associated with the dynamical arrest of a colloidal glass.

Recently, Brambilla et al [125] measures the self-ISF by DLS for a range of volume fraction for a ~10% polydisperse hard sphere suspension. In that study they also perform a numerical simulation of a 50:50 binary mixture of hard spheres of diameter $d$ and $2d$. They found a full decay of the ISF and therefore an absence of dynamical arrest for volume fractions up to $0.597$ as well as an absence of ageing behaviour, thus claiming they are measuring “equilibrium dynamics”. They also found a divergence of the relaxation time - obtained by applying a stretched exponential fit to the slow decay of the ISF – for both experiments and simulation at approximately a volume fraction of 0.64, suggesting that the “MCT transition is generally avoided in colloidal materials, just as in molecular glass formers”. Many complex aspects of this work are questionable:

First, although the solvent in which particles are suspended is not mentioned in this paper, it
is presumably a mixture of Decalin and Tetralin. We know that multiple scattering occurs in such particle suspensions. Effects of multiple scattering can play an important role, especially at high volume fractions. As multiple scattering increases with volume fraction, the $\phi$-dependency of the relaxation time will be influenced and the delicate exponential fit and volume fraction of divergence will be affected.

Second, the high polydispersity (10%) of this experimental hard sphere suspension prevents crystallisation for months at any volume fraction, which makes impossible the determination of the effective volume fraction by observation of the freezing and/or melting volume fraction (as in section 3.1.4). Instead, Brambilla et al. [125] smartly compared the short-time self-diffusion coefficient obtained from DLS to theoretical calculations. However, this yields an uncertainty of the effective volume fraction of about 5%, which is quite enormous in the context of their claims. Also we know that the determination of an accurate value of the short-time diffusion coefficient requires the calculation of the time-dependent diffusion coefficient $D(q,\tau)$, which requires a numerical derivative and adds noise. An alternative is to apply linear fits of slope one to the width function $w(q,\tau)$. Unfortunately, Brambilla et al. [125] do not specify the way they calculate the short-time self-diffusion coefficient. However, the uncertainty of the determination of the short time diffusion coefficient should also be added to the uncertainty (5%) in the effective volume fraction.

Third, Brambilla et al. [125] measure the coherent ISF at $qR=6.1$ where $S(q)\approx 1$. They assume that the coherent and self ISF are equal for scattering vectors where $S(q)\approx 1$. This smart method was inspired from previous findings of Pusey et al [139] who show that approximation was satisfied only at short times. Brambilla et al. [125] have applied this approximation to the entire time window and not only at short-time. However, the results obtained in this thesis question this approximation. In fact we show clearly that coherent and self ISF are only equal at $\phi_g$. This is seen through the analysis in chapter 4 and especially in Figure 4.18. However, we will accept as a “big” approximation that Brambilla et al. [125] measure the self-ISF.

However, the fact that such high a polydispersity system is ergodic at such high volume fractions (up to 0.597) – ergodicity shown by the full decay of the ISF – is in agreement with the results of section 5.3, first observed by Williams et al. [102]. We explain the fact that Brambilla et al. [125] do not observe a glass transition by the fact that they have such a high
polydispersity. The main result of section 5.3 is that introducing a second component in a one component colloidal glass – and so simulating a higher polydispersity – allows a full decay of the ISF and so restores ergodicity. In the present study, we also show that the presence of a second component removes aging behaviour, characteristic of samples with $\phi > \phi_g$. This result explains the observation of “equilibrium dynamics” by Brambilla et al. [125] for samples with volume fractions up to 0.597. To conclude, lack of a glass transition for the ~10% polydisperse hard sphere suspension used by Brambilla et al. [125] is simply due to a high polydispersity, high enough that a first order transition (freezing transition) is not observed at any volume fraction.
In this chapter the coherent ISFs for colloidal glasses \((\phi \geq \phi_g)\) are presented as functions of waiting time following the quench. The aim of this chapter is to identify the mechanisms responsible for the ageing behaviour observed in colloidal glasses, which are both non-ergodic and non-stationary. These characteristics make dynamic measurements a challenge, and sophisticated experimental methods are needed. This is achieved in the current work by combining the PvM method [115] and the Echo DLS technique [129] as detailed in chapter 3.

We will quantify the ageing at several scattering vectors, and study the effects of volume fraction and polydispersity on the ageing behaviour of colloidal glasses. In section 5.1, we quantify the ageing via two analyses (the ISF and the stretching index) at several \(qR\) values for a volume fraction of \(\phi=0.58\). Then we present the effect of volume fraction on the ageing behaviour in section 5.2. Finally we expose the effect of polydispersity in section Error! Reference source not found. by studying the ageing behaviours of binary mixtures of two different sized particles.

In an attempt to characterise and identify the mechanisms driving the dynamical ageing behaviour, we systematically apply two analyses to the data:

(i) The first consists of studying the waiting time dependence of the ISF in the delay-time window corresponding to the slow decay of the ISF.

(ii) The second consists of studying the waiting time dependence of the ISF at the crossover (inflection point) between the fast and the slow processes. In particular, we represent the waiting time dependence of the stretching index \(\nu_s(q)\) and delay time \(\tau_m(q)\) introduced previously. From this analysis, an ageing index \(\zeta\) can be extracted. Providing that this ageing index \(\zeta\) is well defined, this analysis allows the quantification of the ageing process, and the identification of the mechanisms driving the ageing process.

These measurements are extremely time consuming, with a single ageing measurement taking up to 1 week. In order to make the experiments manageable in a finite time, different particle suspensions were used for different aspects of the experiments, as detailed in Table 5.1.
Effect of scattering vector (XL52) at $\phi = 0.58$

<table>
<thead>
<tr>
<th>$\theta$</th>
<th>qR</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>2.01</td>
</tr>
<tr>
<td>60</td>
<td>2.93</td>
</tr>
<tr>
<td>75</td>
<td>3.57</td>
</tr>
<tr>
<td>90</td>
<td>4.15</td>
</tr>
</tbody>
</table>

Effect of volume fraction (XL63)

<table>
<thead>
<tr>
<th>$\phi$</th>
<th>qR</th>
</tr>
</thead>
<tbody>
<tr>
<td>$0.563;(-\phi_g)$</td>
<td>1.86, 2.71, 3.30, 3.84</td>
</tr>
<tr>
<td>$0.574$</td>
<td>3.30</td>
</tr>
<tr>
<td>$0.584$</td>
<td>2.71, 3.30, 3.84</td>
</tr>
<tr>
<td>$0.600$</td>
<td>1.86, 2.71, 3.30, 3.84</td>
</tr>
</tbody>
</table>

Effect of polydispersity (XL52/XL48) at $\phi=0.58$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA1</td>
<td>100% XL52</td>
</tr>
<tr>
<td>SA2</td>
<td>95% XL52 + 5% XL48</td>
</tr>
<tr>
<td>SA3</td>
<td>90% XL52 + 10% XL48</td>
</tr>
<tr>
<td>SA4</td>
<td>80% XL52 + 20% XL48</td>
</tr>
</tbody>
</table>

Table 5.1: Details of samples used for the dynamic measurements.

### 5.1 Manifestations of ageing at different scattering vectors: XL52

#### 5.1.1 Coherent ISF of a colloidal glass ($\phi=0.58$)

Figure 5.1 (top) shows typical ISFs at $\phi=0.58$ for several waiting times at qR=3.57, near the primary maximum in the static structure factor $S(q)$. Figure 5.1 (bottom) shows the ISF for values of qR around the peak of $S(q)$, for two waiting times, $t_w=10h$ ($t_w/\tau_B\sim1.9*10^6$) and $t_w=120h$ ($t_w/\tau_B\sim2.2*10^7$). The horizontal lines are the non-ergodicity parameters measured by the PvM method. The prediction of $S(q)$ from Percus-Yevick, considering a polydispersity of 6% (XL52), is shown as an inset in Figure 5.1, where the points correspond to the qR values where experiments are performed.
Figure 5.1: The ISF (top) for the waiting times indicated at qR=3.57 in the vicinity of the peak of $S(q)$ and (bottom) for $t_w=10h$ and 120h at the qR values indicated. Horizontal lines are the corresponding non-ergodicity factors $f(q,\infty)$ from the PvM method. The inset in (a) shows (left axis) $f(q,\infty)$ and (right axis) $S(q)$ from Percus-Yevick predictions with a polydispersity of 6%, as functions of qR.
In all cases a plateau separates a fast process, with no apparent dependence on the waiting time (more details in section 5.1.3), and a slow process that stretches out as $t_w$ increases. As mentioned previously, the fast process is commonly associated with local motion, while the slow process is commonly associated with structural rearrangements of the particles. In the case where there is non-stationarity (ageing), these processes must be irreversible.

One sees that the ISF’s do not decay to zero in the accessible time window, which, in this case, spans almost nine decades. This contrasts with the results of more complex soft solids, where the measured correlation functions decay fully, or almost fully, in the accessible time window [62, 73, 75-77].

Ideally, to avoid any complication in the physical interpretation of the ageing behaviour, experiments should be done in a time window where dynamics are stationary – i.e. $t_{\text{run}} \ll t_w$. In other words, we would like to avoid any ageing behaviour during the time of an experiment, $t_{\text{run}}$. In practice this is not possible, especially at early ageing times. The experiments performed here are of duration $t_{\text{run}}=10,000$s, measured over 5 days. At early times, significant ageing is occurring during the measurements. To probe the early waiting time dependency, we also performed experiments of $t_{\text{run}}=2,000$s, providing experimental data points at $t_w \sim 0h30$. As will be shown later, these times are sufficient to identify and quantify significant aspects of the ageing process.

The observations of Figure 5.1 raise several questions. First the slow process clearly shows non-stationarity, but does the fast process show stationarity? Second does the crossover between fast and slow processes show stationarity? In quantitative terms, one asks:

(i) does the non-ergodicity factor $f(q, \infty)$ – that allows the quantification of the fraction of structure which is arrested – show non-stationarity?

(ii) Does the stretching index $\nu_c(q)$ – quantifying the “caging” effect – show non-stationarity?

(iii) Does the delay time $\tau_m(q)$ – characterising the time window of the fast process and the beginning of the slow process – show non-stationarity?

(iv) In addition, in chapter 4 it was found that there was $q$ independence of the particle dynamics in the glass region. Does the quantification of the ageing also show $q$ independence?

Each of these points is addressed in the following sub-sections.
5.1.2 Does the non-ergodicity factor show non-stationarity?

The non-ergodicity factor, $f(q, \infty)$, characterises the fraction of the structure which is arrested, and can be determined from the zero-time limit of Eq. 3.13 using the PvM method detailed in section 3.2.2. The PvM method assumes that, for a glass, the space-time number particle density can be decomposed into constant and fluctuating components. The fluctuating component quantifies the local motions of the particles around fixed positions, and the “arrested structure” is quantified by the constant component $f(q, \infty)$.

The measured values of $f(q, \infty)$, obtained by Eq. 3.14, are plotted as open symbols in Figure 5.2 as functions of waiting time at $qR=3.57$ and $t_{\text{run}}=10^3$ s ($\sim 10 \cdot \tau_m^c$). The average value of $f(q, \infty)$ over two decades in waiting time is equal to 0.947 and is represented by the line in Figure 5.2. It is clear that $f(q, \infty)$ does not show systematic variation with waiting time within the noise. Thus stationarity of $f(q, \infty)$ is observed in these experiments.

![Figure 5.2: $t_w$-dependency of the non-ergodicity parameter $f(q, \infty)$ (open symbols) and $f_c(q, \tau_m^c)$ (filled symbols) for XL52 at $qR=3.57$. Line is the average value of $f(q, \infty)$ over the whole waiting time window. Duration time of the experiments is presented in parenthesis.](image)

However, while the fast process shows stationarity, the slow process does not. To the extent that the crossover is a measure of the coupling between the fast and slow processes, one could question the criteria for measuring $f(q, \infty)$. The PvM method assumes that particles have only local motion around fixed positions and so excludes any particle rearrangements, either
reversible or irreversible, during the time of an experiment. As observed in Figure 5.1, such particle rearrangements, whatever their nature, only occur at delay times past the plateau in the ISF \( \tau > \tau_m^{c} \), where the slow ageing process is observed. Thus the PvM method should be applied only to probe the fast process – or fast decay of the ISF \( f(q, \tau < \tau_m^{c}) \) – and so for an experiment duration \( t_{\text{run}} \) approximately equal to delay times up to the plateau in the ISF \( \tau \sim \tau_m^{c} \). This will ensure that the measurements are not affected by the decay of the density fluctuations from the slow process.

To illustrate the effect of \( t_{\text{run}} \) on the results obtained via the PvM method, we show in Figure 5.3 the \( t_w \)-dependency of \( f(q, \infty) \) at \( qR=2.93 \) for three values of \( t_{\text{run}} \): (a) \( t_{\text{run}}=10^2 s \sim \tau_m^{c} \), (b) \( t_{\text{run}}=10^3 s \sim 10 \cdot \tau_m^{c} \) and (c) \( t_{\text{run}}=10^4 s \sim 10^2 \cdot \tau_m^{c} \). In all cases, \( f(q, \infty) \) does not show systematic variation with the waiting time, despite the noise. However one sees that the average value over \( t_w \), \( \langle f(q, \infty) \rangle \), represented by the lines, decreases slightly upon increasing \( t_{\text{run}} \). This result is expected as some slow density fluctuations occur during the time of the experiment for large values of \( t_{\text{run}} \).

We compare, in Figure 5.4, our measurement of \( f(q, \infty) \) to previous work [128] and find consistency between both data sets. In the past, van Megen showed that \( f(q, \infty) \) varies in harmony with the static structure factor and that MCT reproduces quantitatively the \( f(q, \infty) \) values from DLS measurements.
Figure 5.3: Non-ergodicity parameter $f(q, \infty)$ as a function of waiting time for (a) $t_{\text{run}} = 10^2 s \sim \tau_m^c$, (b) $t_{\text{run}} = 10^3 s \sim 10 \cdot \tau_m^c$ and (c) $t_{\text{run}} = 10^4 s \sim 10^2 \cdot \tau_m^c$. $f(q, \infty)$ does not show ageing and $f(q, \tau_m^c)$ shows very little variation with $t_w$ (within $\sim 0.5\%$) and is negligible compared to the variation of $f(q, \tau_{\text{max}})$ as shown in Figure 5.8. Lines are the average over the whole $t_w$ window and values are in legend. Note that the average value of the non-ergodicity parameter $f(q, \infty)$ decreases as the duration time of the experiments increases.
Figure 5.4: Left axis: non-ergodicity factor, \( f(q,\infty) \), as function of qR for our measurements (filled symbols) and previous work [128] (open symbols). Lines are MCT calculations. Right axis: prediction of \( S(q) \) (dashed line) from Percus-Yevick for a polydispersity of 6%. Black filled circles are data from XL52 and other filled symbols from XL63.

The non-ergodicity factor, \( f(q,\infty) \), represents the constant component of the density fluctuations and so quantifies the fraction of the structure which is “arrested”, and, at least from our results, shows stationarity. This agrees with recent observations via confocal microscopy [47, 49] where only weak correlation between structure and dynamical ageing was observed.

The primary result of this analysis – stationarity of the non-ergodicity factor for a hard sphere glass – is in contrast to results reported for attractive hard sphere glasses, where significant non-stationarity of the “measured” non-ergodicity factor \( f^{\text{M}}(q,\infty) = f(q,\tau_m^c) \) was observed [80]. The result also contrasts with a strong ageing behaviour of Laponite glasses in \( f(q,\infty) \), observed by Jabbari-Farouji et al. [89], which exposed a transition from an ergodic state, with \( f(q,\infty)=0 \), at early waiting times, to a non-ergodic state, with \( f(q,\infty)\sim0.8 \), at long waiting times. Those experiments were performed at very low qR, approximately 0.5, while ours are for \( 2 < \text{qR} < 4.15 \). It would be interesting to perform similar experiments at lower qR, however instrument limitations and scattered intensity limit our experiments to qR > 2.0.
experiments may shed further light on the differences observed in the ageing behaviour of the three different systems.

**5.1.3 Does the fast process show non-stationarity?**

To look more closely at whether or not the fast process has a waiting time dependency, the optimal experimental conditions need to be established. The fast process extends from the zero-time limit up to \( \tau_m^c \), the crossover time between fast and slow processes. Thus the delay time range required to probe the fast process is \( \tau \leq \tau_m^c \). However, we need to establish which experimental duration, \( t_{\text{run}} \), should be used, and how many runs are necessary to obtain sufficiently good statistics in a short enough time to study the \( t_{\omega} \)-dependency.

To answer these questions, Figure 5.5 (left) shows the ISF measured by the PvM method for several experimental conditions. We found that 5 independent runs, each corresponding to a different scattering volume, of \( t_{\text{run}} \sim 10 \cdot \tau_m^c \), achieves similar statistical reliability as 450 runs of duration \( t_{\text{run}} \sim \tau_m^c \). We also compare these results, in Figure 5.5 (right), with the Brute Force method by performing 220 runs (each for a different scattering volume) with \( t_{\text{run}} \sim 10 \cdot \tau_m^c \). Again, the statistics are surprisingly good, showing the power of the PvM method for probing the fast process of colloidal glasses (only) with a small number of relatively short experiments.

Figure 5.5: (left) ISF from the PvM method as function of delay time for several values of run number \( n_{\text{run}} \) and duration time \( t_{\text{run}} \) as indicated in parenthesis \( (n_{\text{run}}, t_{\text{run}}) \). Data are shown for \( qR=2.93 \) and a volume fraction of 0.580. (right) Comparison between the PvM and Brute Force method at \( qR=3.57 \), \( t_{\text{run}} = 10^3 \, s \sim 10 \cdot \tau_m^c \) for the number of runs indicated.

After checking that the procedure for obtaining the fast decay of the ISF via the PvM method has sufficiently good statistics, we can now probe whether or not the fast decay of \( f(q, \tau) \) has
a \( t_w \)-dependency. We do so by plotting the ISF obtained via the PvM method as function of delay time for several \( t_w \) in Figure 5.6. Here, we apply averaging of blocks of 10 runs. Despite the noise, no significant trend is observed with waiting time. To characterise precisely the possible \( t_w \)-dependency, we plot, in Figure 5.7, the value of the ISF at delay times of 0.1s, 1s and 10s, as functions of \( t_w \). Clearly, there is no \( t_w \)-dependency in these quantities, confirming the stationarity of the fast decay of the ISF.

Figure 5.6: ISF from the PvM method as function of delay time for several waiting time. Each curve corresponds to an average of 10 runs of \( t_{\text{run}} = 10^3 \text{s} \sim 10^3 \tau_w \) at \( qR=3.57 \).

Figure 5.7: Value of the ISF at the delay times indicated, as functions of waiting time. Each point corresponds to an average of 10 consecutive runs at \( qR=3.57 \). No ageing is observed either around the characteristic time of the fast decay (~0.1s), or the time of overlapping with the echo DLS data (~1-10s). Note the vastly expanded scale.
The data obtained here demonstrates the existence of a fast process, with no apparent \( t_w \)-dependency, spanning from very short-times \(( \tau < \tau_B )\) up to the crossover between the fast and slow processes \(( \tau \sim \tau_m^c )\). In addition, as shown in the previous section, the non-ergodicity factor does not show a \( t_w \)-dependency, and so the average structure does not change as the sample ages. So the only way for the ISF to decay below the non-ergodicity factor – corresponding to the slow process – is through the exchange of particles, which must be irreversible. This is examined in the next section.

### 5.1.4 Ageing of the slow process

In this section we quantify the ageing of the slow process by analysing the ISF itself, first at the longest delay time accessible, \( \tau_{max} \), and then for \( \tau > \tau_m^c \). Despite the limited decay of the ISF, observed in Figure 5.1, the ageing process can still be quantified by plotting, in Figure 5.8, the ISF at the upper limit of the time window, \( f(q, \tau_{max}, t_w) \), as a function of \( t_w \) for several \( qR \) values. At all scattering vectors probed, around the peak of \( S(q) \), \( f(q, \tau_{max}, t_w) \) follows a power law of form:

\[
f(q, \tau_{max}, t_w) = A(q) \left[ 1 - \left( \frac{t_w}{t_0} \right)^{-b} \right]
\]

Eq. 5.1

The power law fits are represented by the lines in Figure 5.8. At the structure factor peak, the exponent \( b \sim 0.66 \) and timescale \( t_0 \sim 200 s \). The values of these parameters scale approximately with the structure factor, varying by 35\% (for \( b \)) and 50\% (for \( t_0 \)) over the \( q \) range studied and are presented in Table 5.2 together with the measured non-ergodicity factors, \( f(q, \infty) \). The interesting point here is that the value of the amplitude \( A(q) \) agrees with \( f(q, \infty) \) to within 2\%. This is illustrated by the horizontal lines in Figure 5.8.
Figure 5.8: (Left axis) $f(q, \tau_{\text{max}}, t_w)$ (filled symbols) and (right axis) plateau height $f(q, \tau_m^c)$ (open symbols) as functions of the waiting time for several values of $qR$. $\tau_{\text{max}}/\tau_B \sim 4.5 \cdot 10^5 \sim 8200s$ is the upper limit of the time window. Lines are power law fits to the data. The non-ergodicity factor, $f(q, \infty)$, from the PvM method Eq. 3.14, is shown as horizontal lines.

Table 5.2: Plateau height $f(q, \tau_m^c)$, non-ergodicity factor $f(q, \infty)$, and parameters of the power law fits from Eq. 5.1. Note that $A(q)$, $f(q, \infty)$, and $f(q, \tau_m^c)$, agree to within less than 2%.
Figure 5.9 shows the $t_w$-dependency of $f(q, \tau > \tau^c_m; t_w)$ for several delay times $\tau > \tau^c_m$ and qR values. For all delay times, $\tau > \tau^c_m$, $f(q, \tau > \tau^c_m; t_w)$ follows a power law of form Eq. 5.1, represented by the dashed lines. For qR=3.57, data were collected at several different values of $t_{run}$, in order to examine the early waiting time dependency, and so increase the reliability of the parameters in the power law fit. The amplitude $A(q)$, represented as functions of delay time in Figure 5.10, does not show any significant variations with delay time and agrees with the non-ergodicity factors, $f(q, \infty)$, to within approximately 2%. The fact that $A(q) \sim f(q, \infty)$ demonstrates that the ISF approaches the non-ergodicity factor algebraically for all delay times $\tau > \tau^c_m$. The ageing behaviour is most pronounced at $\tau = \tau_{\text{max}}$ but almost imperceptible at $\tau = \tau^c_m$. 
Figure 5.9: $f(q, \tau > \tau_m^c, t_w)$ as a function of waiting time, $t_w$, for the delay times $\tau / \tau_B$ and qR values indicated. Dashed lines are power law fits to the data. The non-ergodicity factor $f(q, \infty)$ is also represented by horizontal lines. For data at qR=3.57, several series of experiments with different duration time, $t_\text{run}$, have been performed: 2 series with $t_\text{run} = 2000s$ and $t_\text{run} = 4000s$ during the first 10h after the quench; and 3 series with $t_\text{run} = 10000s$ and initial waiting times 0h40, 2h and 3h. This provides more points at early waiting times and so
enables more reliable fits. For the others qR values, data are from 1 series, with $t_{\text{run}}=10000\text{s}$ and an initial waiting time 0h40.

![Figure 5.10: Amplitude $A(q)$ of the power law fit (Eq. 5.1) as a function of delay time for several qR values. Lines and dashed lines are $f(q,\infty)$ and $f(q,\tau_m^*)$ respectively.](image)

While determination of $A(q)$ from the fit (Eq. 5.1) is robust, the exponent $b$ and timescale $t_o$ are subject to significant noise. With the present data, we cannot associate any significance to these parameters and do not discuss them further.

### 5.1.5 Ageing at the crossover (analysis of the inflection point).

In this section, we quantify the ageing behaviour by characterising the $t_w$-dependency of the stretching index, $v_c(q)$ via the width function, previously introduced in chapter 4. It was found in chapter 4 that the complement, $c_c(q)$, of $v_c(q)$, increases and its q-dependency decreases upon approaching the glass transition. We present the width function for $\phi = 0.58$ at four qR values around the peak of $S(q)$ in Figure 5.11. If the relaxation of the particle number density fluctuations were diffusive, $w(q,\tau)$ would increase in proportion to $\tau$, and its logarithmic slope, $n(q,\tau)$ – defined from Eq. 4.3 in chapter 4, and presented in the insets of Figure 5.11 – would be one, for all delay times. Obviously, this is far from the case. It is evident from the insets in Figure 5.11 that $n(q,\tau)$ has a minimum, $v_c(q)=\min[n(q,\tau)]$ at
that deepens with age. As mentioned in the previous section, we identify \( \tau_m^c(q) \) as the crossover time between the fast process, \( f(q, \tau < \tau_m^c; t_w) \), and the slow process, \( f(q, \tau > \tau_m^c; t_w) \), and the stretching index, \( \nu_c(q) \), as a measure of the coupling between them. To better quantify the minima in \( n(q, \tau) \), we applied a polynomial fit in the vicinity of the minima. These are shown as dashed lines in the insets of Figure 5.11.
Figure 5.11: Shows the width function (Eq. 4.1) as a function of delay time at qR and waiting times indicated. Inset: $n(q, \tau)$ (Eq. 4.3) in the echo DLS range, where the inflection is observed.
**Stretching index $v_c(q)$ and delay time $\tau^c_m(q)$**

Figure 5.12 shows that the $t_w$-dependency of $v_c(q)$ can be described by a power law;

$$v(q) = \left( \frac{t_w}{t_x} \right)^{-\zeta}.$$  \hspace{1cm} \text{Eq. 5.2}

The timescale $t_x$ and exponent $\zeta$ are presented in Table 5.3. The timescale $t_x$ shows little variation with $q$ and follows approximately $S(q)$ as shown in the inset of Figure 5.12. The exponent $\zeta=0.20\pm0.02$ shows no variation with $q$. We define $\zeta$ as our second ageing index, which is indicative of the strength of the ageing process at the crossover between the fast and slow processes.

![Figure 5.12: The stretching index, $v_c(q)$, as a function of the waiting time for several scattering vectors. Lines are power law fits (Eq. 5.2) to the data. Inset shows the Percus-Yevick structure factor (left axis) for a polydispersity of 6% and timescale $t_x$ (right axis) of the power law fits as functions of qR.](image)
<table>
<thead>
<tr>
<th>qR</th>
<th>Amplitude t_x (h)</th>
<th>Ageing exponent ζ</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>±.001</td>
<td>± 0.02</td>
</tr>
<tr>
<td>2.01</td>
<td>0.037</td>
<td>0.18</td>
</tr>
<tr>
<td>2.93</td>
<td>0.049</td>
<td>0.20</td>
</tr>
<tr>
<td>3.57</td>
<td>0.080</td>
<td>0.20</td>
</tr>
<tr>
<td>4.15</td>
<td>0.056</td>
<td>0.20</td>
</tr>
</tbody>
</table>

Table 5.3: Values of the amplitude t_x and exponent ζ of the power law fits (Eq. 5.2) of the t_w-dependency of the stretching index ν_c(q).

The delay time, τ_m^c(q), at the crossover, represented as a function of t_w in Figure 5.13, shows a t_w-dependency and increases by almost an order of magnitude as the sample ages. Whether or not τ_m^c(q) reaches a plateau at long t_w is uncertain. By contrast with the stretching index, τ_m^c(q) shows no variation with scattering vector. This is consistent with findings of chapter 4 showing that τ_m^c(q) loses its q-dependency upon approaching φ_g..

Figure 5.13: Delay time, τ_m^c(q), at the crossover between the fast and slow processes as functions of waiting time. τ_m^c(q) increases as the sample ages and eventually becomes approximately stable at long waiting times. For clarity, error bars are only indicated for one series of experiments.
How well does \( f(q,\tau_m^c) \) isolate the fast stationary processes: \( f(q,\tau_m^c) = f(q,\infty) \)? We compare the non-ergodicity factor, \( f(q,\infty) \), obtained from the PvM method, with the actual value of the ISF, \( f(q,\tau_m^c) \), at the crossover between the fast and slow processes. Both \( f(q,\infty) \) and \( f(q,\tau_m^c) \) are represented as functions of \( t_w \) in Figure 5.2 and Figure 5.3. Despite the noise, \( f(q,\infty) \) and \( f(q,\tau_m^c) \) agree to within \( \sim1\% \). However, while \( f(q,\infty) \) does not show any significant ageing, \( f(q,\tau_m^c) \) shows a very weak \( t_w \)-dependency. However, the \( t_w \)-dependency of \( f(q,\tau_m^c) \), within \( \sim0.5\% \), is negligible in comparison to that of \( f(q,\tau_{\text{max}}) \) shown in Figure 5.8.

Note that by changing the duration time, \( t_{\text{run}} \), of an experiment and applying the PvM method, there is a relative systematic change between \( f(q,\infty) \) and \( f(q,\tau_m^c) \). The average value of \( f(q,\infty) \) changes weakly with \( t_{\text{run}} \). At \( t_{\text{run}} \sim \tau_m^c \) (Figure 5.3a), \( f(q,\infty) \) is slightly higher than \( f(q,\tau_m^c) \) - here all density fluctuations due to the fast process are not entirely sampled during \( t_{\text{run}} \sim \tau_m^c \). At \( t_{\text{run}} \sim 10 \cdot \tau_m^c \) (Figure 5.3b), both \( f(q,\infty) \) and \( f(q,\tau_m^c) \) match extremely well, despite the very weak \( t_w \)-dependency of \( f(q,\tau_m^c) \). Here, all density fluctuations due to the fast process are probed during \( t_{\text{run}} \sim 10 \cdot \tau_m^c \) and the density fluctuations due to the slow-ageing process are negligible. Finally, at \( t_{\text{run}} \sim 10^2 \cdot \tau_m^c \) (Figure 5.3c), density fluctuations due to the slow-ageing process become significant and as a result, \( f(q,\infty) \) is lower than \( f(q,\tau_m^c) \).

To summarize this section, the ISF at the crossover \( f(q,\tau_m^c) \) agrees with the non-ergodicity factor \( f(q,\infty) \) and does not show significant ageing in comparison to \( f(q,\tau_{\text{max}}) \). The stretching index \( \nu_c(q) \) and delay time \( \tau_m^c(q) \) show strong ageing behaviour. The \( t_w \)-dependency of \( \nu_c(q) \) can be described by a power law, with an exponent (or ageing index) which is independent of scattering vector, with \( \zeta=0.20\pm0.02 \). The delay time \( \tau_m^c(q) \) shows an increase with \( t_w \) over almost a decade and eventually appears to become constant.
5.2 *Effect of volume fraction on the ageing process: XL63*

The above analysis was carried out at a single volume fraction. In order to determine if the trends discussed above are general, we need to establish that the ageing behaviour is qualitatively the same at other volume fractions in the glassy region. For these experiments, we used a different particle suspension: XL63, whose properties are tabulated and discussed in chapter 3. XL63 has a refractive index slightly closer to cis-decalin, making it suitable for experiments at higher volume fractions. It also has a slightly higher polydispersity, 8-9%, than XL52 which is 6%. Experiments were performed at $\phi=0.563$, 0.574, 0.584 and 0.600. Note that the sample at $\phi=0.563\sim\phi_g$ is in the (narrow) glass transition region.

The ISFs are presented as functions of delay time for a range of waiting times in Figure 5.14 for $qR=3.30$. The insets show the ISF for two separates waiting times and several $qR$ values. The non-ergodicity factor, $f(q,\infty)$, is shown as horizontal lines. As found in section 5.1, in all cases a plateau separates a fast process with no apparent $t_w$-dependency and a slow process that shows a strong $t_w$-dependency for $\phi \geq 0.584$. There is only a weak $t_w$-dependency at $\phi=0.563$. 


Figure 5.14: ISF versus delay time for a range of waiting times and qR values as indicated for volume fractions of (a) 0.563−qg, (b) 0.574, (c) 0.584 and (d) 0.600. Horizontal black lines are the measured non-ergodicity factors. Insets show the ISF for several qR values at early and long waiting times.
The $t_w$-dependency of the non-ergodicity factor, $f(q,\infty)$, is presented in Figure 5.15 at $qR=3.30$. As previously found in section 5.1, $f(q,\infty)$ does not show any ageing behaviour within the noise for all volume fractions.

Figure 5.15: $t_w$-dependency of the (open symbols) non-ergodicity factor, $f(q,\infty)$, and (filled symbols) ISF $f(q,\tau_m^c)$ at the crossover between the fast and slow processes for (circles) $\phi=0.563$, (squares) $\phi=0.574$, (triangles) $\phi=0.584$ and (diamonds) $\phi=0.600$. Lines are averages over the waiting times of the measured $f(q,\infty)$.

5.2.1 Ageing of the slow process: effect of volume fraction

As in section 5.1, we examine the $t_w$-dependency of $f(q,\tau)$ and this is shown in Figure 5.16 at $qR=3.30$, for the volume fractions mentioned above. At $\phi=0.563$~$\phi_g$, very little ageing is observed at short $t_w$ and the ISF reaches stationarity at long $t_w$ – $f(q,\tau_{\text{max}};t_w)$ cannot be described by a power law – and do not tend towards the non-ergodicity factor (black line) suggesting that the ISF will fully decay to zero at longer delay times, not accessible in our experimental time window. At $\phi=0.574$, 0.584, 0.600 $> \phi_g$, the ISF shows a strong $t_w$-dependency and can be described by a power law as shown in dashed lines in Figure 5.16b, c, and d.
Figure 5.16: $t_w$-dependency of $f(q,\tau)$ at $qR=3.30$ for (a) $\phi=0.563$, (b) $\phi=0.574$, (c) $\phi=0.584$ and (d) $\phi=0.600$. Horizontal lines are the non-ergodicity factors $f(q,\infty)$. 
The amplitude $A(q)$ of the power law fits are represented as functions of delay time for these volume fraction in Figure 5.17 and compared to the non-ergodicity factor (note that for $\phi=0.563$ $A(q)$ is taken as the average over the last $t_w$ points). At $\phi=0.574$, 0.584, 0.600 $> \phi_g$, $A(q) \sim f(q, \infty)$ at all delay times $\tau > \tau_m^c$ and thus the ISF approaches the non-ergodicity factor algebraically for all delay times $\tau > \tau_m^c$. This clearly not the case for $\phi=0.563$.

Figure 5.17: Amplitude $A(q)$ of the power law fit from Eq. 5.1 as functions of delay time at $\phi=0.563$, 0.574, 0.584 and 0.600 at qR=3.30. The non-ergodicity factor, $f(q, \infty)$, is shown as lines.

### 5.2.2 Ageing at the crossover

Figure 5.18 shows the $t_w$-dependency of (left column) the stretching index $\nu_c(q)$ and (right column) the delay time at the crossover $\tau_m^c(q)$. 
Figure 5.18: (Left column) stretching index $\nu_c(q)$ and (right column) delay time $\tau_m(q)$ at (a) $\phi = 0.563$, (b) $\phi = 0.574$, (c) $\phi = 0.584$ and (d) $\phi = 0.600$ for the qR values indicated. Lines are power law fits to the data.

Considering first $\phi = 0.563-\phi_g$, it is clear that the stretching index shows some $t_w$-dependency at early waiting times, but it reaches stationarity at long $t_w$ - a power law cannot describe the
The $t_w$-dependency of $\nu_c(q)$. The delay time $\tau_m^c(q)$ does not show any systematic variation with $t_w$, though there appears to be some $q$-dependency.

For volume fractions above $\phi_g$, the stretching index exhibits a strong $t_w$-dependency that can be described by a power law. There is some $q$-dependency of $\nu_c(q)$, although it is small and approximately follows $S(q)$. However, $q$-dependency of $\tau_m^c(q)$ observed at $\phi_g$ is lost at higher volume fractions ($\phi=0.584$ and 0.600). Moreover, $\tau_m^c(q)$ also shows a $t_w$-dependency, almost imperceptible at $\phi=0.574$, but increasing to over half a decade at $\phi=0.584$ and almost a decade at $\phi=0.600$. These observations confirm the results obtained in chapter 4 and section 5.1.

We compare the $t_w$-dependency of $\nu_c(q)$ and $\tau_m^c(q)$ at several volume fractions in Figure 5.19 at qR=3.30. Lines are power law fits to the data. For clarity, offsets have been applied to the data in Figure 5.19 (top). Clearly this figure shows that beyond the glass transition there is no change in the slope of the fits. This is confirmed by the values of the ageing index $\zeta$ presented in Table 5.4, which show no variation with either scattering vector or volume fraction. Figure 5.19 (bottom) shows the delay time $\tau_m^c(q)$, which clearly increases with volume fraction above the glass transition, but more importantly its $t_w$-dependency also increases with $\phi$.

<table>
<thead>
<tr>
<th>qR</th>
<th>$\zeta$ at $\phi=0.563$</th>
<th>$\zeta$ at $\phi=0.574$</th>
<th>$\zeta$ at $\phi=0.584$</th>
<th>$\zeta$ at $\phi=0.600$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.86</td>
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<td>NA</td>
<td>NA</td>
<td>-0.21</td>
</tr>
<tr>
<td>2.71</td>
<td>$\rightarrow 0$</td>
<td>NA</td>
<td>-0.21</td>
<td>-0.19</td>
</tr>
<tr>
<td>3.30</td>
<td>$\rightarrow 0$</td>
<td>-0.20</td>
<td>-0.21</td>
<td>-0.23</td>
</tr>
<tr>
<td>3.84</td>
<td>$\rightarrow 0$</td>
<td>NA</td>
<td>-0.23</td>
<td>-0.20</td>
</tr>
</tbody>
</table>

Table 5.4: Ageing index $\zeta$ (Eq. 5.1) for two volume fractions and several qR values.

The $t_w$-dependency of the ISF at the crossover, $f(q,\tau_m^c)$, is presented in Figure 5.15 together with the non-ergodicity factor, $f(q,\infty)$. As previously found in section 5.1, both $f(q,\infty)$ and $f(q,\tau_m^c)$ agree to within 1% at $\phi=0.563$ and 0.600, and to within 3% at $\phi=0.584$. While $f(q,\infty)$ does not show any ageing behaviour within the noise, $f(q,\tau_m^c)$ does show some
ageing at $\phi=0.574$ and $0.600>\phi_g$ but not at $\phi=0.563 \sim \phi_g$. It appears stronger at 0.574 (~2.2%) than at 0.600 (~0.8%), however, these variations are probably within the experimental noise.

Figure 5.19: Effect of the volume fraction on the $t_w$-dependency of (top) the stretching index $v_c(q)$ and (bottom) the delay time $\tau_m(q)$ at the crossover. Lines are power law fits to the data.
5.3 Ageing of Binary mixtures

This section aims to look at the effect of the polydispersity on the ageing process. We do so by performing experiments using the protocols developed above, but using a binary mixture to change the polydispersity. The two particles used are XL52 (R=200nm) containing a small amount of smaller particles XL48 (R=120nm) while maintaining the total volume fraction at $\phi = 0.58$, which is well into the glass region for pure XL52. We perform these experiments at $T=23^\circ C$ where the smaller particles (XL48) are optically matched with the solvent, and so the fluctuations of the scattered intensity, measured through the PvM method and Echo DLS, only depend on the motion of the larger particles (XL52) (see section 3.1). This allows us to obtain the partial ISF $f_{11}(q,\tau)$, for the larger particles. The compositions of the samples – SA1, SA2, SA3, and SA4 – are presented in Table 5.1 at the beginning of this chapter. These samples were used in previous work [102], where each of the partial ISFs were measured. In that work it was shown that the addition of the second component leads to a melting of the glass, however that work did not examine the ageing process. The question posed here is: Does the addition of the second component affect the $t_w$-dependency of the ISF, stretching index $\nu_c(q)$ and/or $\tau_m(q)$? and thus the ageing index $\zeta$?

Figure 5.20 shows the ISF for SA1, SA2, SA3 and SA4 at $qR=3.57$ for a range of waiting times. It is clear that the $t_w$-dependency of the ISF at delay times $\tau > \tau_m$ changes dramatically as the second component is added. For SA1, as seen in section 5.1, the ISF approaches the non-ergodicity factor algebraically. For SA2 and SA3, whether or not the samples reach stationarity is not clear in the time window available. However, it is clear from Figure 5.20 that the ISF of SA4 reaches stationarity, and almost fully decays, in our experimental time window, by contrast with SA1, SA2 and SA3. Experiments performed at $qR=2.93$ showed similar results. For illustration the ISF’s at $qR=2.93$ and 3.57 at early waiting times are represented in the left insets of Figure 5.20.
Figure 5.20: ISF as function delay time for (a) SA1, (b) SA2, (c) SA3 and (d) SA4 at $\phi=0.58$ and qR~3.57 for waiting times as indicated. Inset on the left shows the ISF as function of delay time at several qR values and one waiting time as indicated. The non-ergodicity factors, $f(q, \infty)$, are represented by horizontal lines. Inset on right in (a) shows $f(q, \infty)$ as a function of qR along with $S(q)$. 
Figure 5.21 shows the effect of adding a second component on the long waiting time ISF at (a) $qR=2.93$ and (b) $qR=3.57$. In both cases, dynamical arrest is not observed for the highest ratio of smaller particles (SA4). This confirms the observation of Williams et al. [102] that high polydispersity melts the glass. The ISF of SA4 sample shows stationarity and (almost) a full decay to the noise floor. Clearly not only the ageing process, but also whole dynamics – fast and slow processes – are affected by adding smaller particles.

Figure 5.21: ISF as function of delay time for “aged” samples SA1, SA2, SA3 and SA4 for $\phi=0.58$ at (a) $qR=3.57$ and (b) $qR=2.93$. $f(q,\infty)$ is represented by horizontal lines.
These two components systems are subject to increased uncertainty in volume fractions. However, the q-dependency of the ISF, characterised in part by the $f(q, \infty)$, is consistent with predictions, from Percus-Yevick theory for binary mixtures, as shown by Williams et al. [102].

One could also argue that these observations are due to depletion attractions due to the presence of the smaller particles (XL48). However, the fact that SA4, the sample in which ratio of the smaller particles is largest, does not show ageing behaviour contrasts with the strong ageing behaviour observed previously in attractive glasses [80]. Also the dimensionless range of the nominal depletion attraction is $\xi \sim r_g / R$ equal to 0.6 in our systems is far away from the attractive glass ~0.09 used there [80].

To better illustrate these observations – that the ageing scenario changes when adding a second component – we first look at the $t_w$-dependency of the ISF at all delay times $\tau > \tau_*$. This is shown in Figure 5.22. Clearly adding a second component affects the $t_w$-dependency of the slow decay of the ISF, with a power law describing the $t_w$-dependency for SA1, SA2 and SA3 samples. However, the ISF of SA4 shows clear stationarity and so power laws fits are not applicable.

Figure 5.23 shows the amplitude $A(q)$ of the power law fits as functions of delay time for the four samples together with the non-ergodicity factor via $f(q, \infty)$ (lines). For SA1, $A(q) \sim f(q, \infty)$, so the ISF approaches its ideal “aged” glass algebraically. By increasing the ratio of the second component, deviations between $A(q)$ and $f(q, \infty)$ are observed, which are better illustrated on the expanded scale in the inset of Figure 5.23. Despite this variation, the ISFs from SA2 and SA3 can be described by a power law. This clearly shows that after the quench the SA2 and SA3 samples approach their own “fully” aged state algebraically. Whether or not the state they approach is an “ideal” glass – where particles perform local motion about fixed positions and reversible particle rearrangements are allowed but irreversible particle rearrangements are not – is open to question. By contrast SA4 reaches a stationary state that fully relaxes.
Figure 5.22: $t_w$-dependency of the ISF, at delay times $\tau > \tau_m$ as indicated, for (a) SA1, (b) SA2, (c) SA3 and (d) SA4 at $\phi=0.58$ and $qR=3.57$. Dashed lines are power law fits to the data and horizontal lines are $f(q, \infty)$. 
Figure 5.23: (a) Amplitude $A(q)$ (from Eq. 5.1) as functions of delay time for SA1, SA2, SA3 and SA4 at $\phi=0.58$ and $qR=3.57$. Inset in (a) shows an expanded y-axis scale. Lines are the non-ergodicity factors, $f(q,\infty)$.

As clearly seen in Figure 5.20, the fast decay of the ISF $f(q,\tau < \tau^*_m)$ – that is the fast process – is also affected by adding a second component but still remains stationary for all samples probed here. The latter is illustrated in Figure 5.24 by plotting the $t_m$-dependency of the fast decay of the ISF at $\tau=0.1s$ and $1s$ for all four samples of $qR=3.57$. 
Figure 5.24: \( t_w \)-dependency of the fast process at (a) \( \tau = 0.1 \text{s} \) and (b) \( \tau = 1 \text{s} \) for SA1, SA2, SA3 and SA4 at \( \phi = 0.58 \) and \( q_R = 3.57 \). Dashed lines are averages over the waiting time.

Figure 5.25 shows the \( t_w \)-dependency of non-ergodicity factor, either via \( f(q, \infty) \) or \( f(q, \tau_m^s) \), for the four samples at \( q_R = 3.57 \). \( f(q, \tau_m^s) \) shows no ageing to within 0.5% and agrees with \( f(q, \infty) \) very well within 1% for SA1, SA2 and SA3 and within 4% with SA4.
Figure 5.25: $t_w$-dependency of the non-ergodicity factor, either $f(q,\infty)$ (open symbols) or $f(q,t_w)$ (filled symbols) for (a) SA1, (b) SA2, (c) SA3 and (d) SA4 at $\phi=0.58$ and $qR=3.57$. Lines are the average over $t_w$ of $f(q,\infty)$. 

\[ f(q,\tau^c_m) \] or \[ f(q,\infty) \] or \[ f(q,\tau^c_m) \] or \[ f(q,\infty) \] \[ f(q,\tau^c_m) \] or \[ f(q,\infty) \] \[ f(q,\tau^c_m) \] or \[ f(q,\infty) \] \[ f(q,\tau^c_m) \] or \[ f(q,\infty) \]
Figure 5.26 shows the $t_w$-dependency of the stretching index at $\phi=0.58$ and $qR=2.93$ and 3.57 respectively. For clarity, offsets have been applied to the data. The stretching index $v_r(q)$ follows a power law decay with $t_w$ for SA1, SA2 and SA3. Power law fits are represented by lines. However, $v_r(q)$ does not show any ageing behaviour for SA4. The values of the ageing index $\zeta$ of the power law fits are presented in Table 5.5. It is clear that the $t_w$-dependency of $v_r(q)$ is strongly affected when adding a second component and this is quantified through significant changes in the ageing index $\zeta$, shown in Table 5.5. $\zeta$ is approximately equal to 0.20 for a relatively low polydispersity (SA1) and 0 for a relatively high polydispersity (SA4).

The $t_w$-dependency of the delay time $\tau_m^c(q)$ is also presented in Figure 5.26. $\tau_m^c(q)$ is also strongly affecting when adding a second component. For SA1, an increase of $\tau_m^c(q)$ over almost a decade is observed while $\tau_m^c(q)$ shows stationarity for SA2, SA3 and SA4. Also $\tau_m^c(q)$ significantly decreases as the ratio of smaller particles increases. To the extent that we are only observing the dynamics of the bigger particles (XL52), the presence of the smaller particles facilitates or “speeds up” the motion of the bigger particles - i.e $\tau_m^c(q)$ decreases when the ratio of smaller particle increases. This is consistent with recent observations obtained from confocal microscopy [50].

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\zeta$ at qR=2.93</th>
<th>$\zeta$ at qR=3.57</th>
</tr>
</thead>
<tbody>
<tr>
<td>SA1</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>SA2</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>SA3</td>
<td>0.09</td>
<td>0.14</td>
</tr>
<tr>
<td>SA4</td>
<td>$\rightarrow 0$</td>
<td>$\rightarrow 0$</td>
</tr>
</tbody>
</table>

Table 5.5: Values of the ageing exponent $\zeta$ of the power law fits (from Eq. 5.2) for SA1, SA2, SA3 and SA4 at qR=2.93 and qR=3.57.
Figure 5.26: $t_w$-dependency of the stretching index $\nu_c(q)$ and delay time $\tau_m^c(q)$ at the crossover for SA1, SA2, SA3 and SA4 at $\phi=0.58$ for (left column) $qR_1=2.93$ and (right column) $qR_1=3.57$ where $R_1$ is the radius of the bigger particles (XL52).

The results presented in this section obtained from binary mixtures of XL52 and XL48 leads to three different scenarios appearing in the particle dynamics. This is first apparent from Figure 5.20 and Figure 5.22 but better characterised in Figure 5.23.

At low polydispersity (SA1) – here obtained by a one component system as opposed to a binary mixture – the system approaches the ideal “aged” glass algebraically, the state in which particles only perform local motion around fixed positions and where reversible and irreversible particle rearrangements are prohibited.

By increasing the polydispersity (SA2 and SA3) – adding a second component – the system approaches some final state algebraically – however, this state appears to be one which allows
local motion around fixed positions as well as reversible particle rearrangements, but where irreversible particle rearrangements do not occur (ie there is no ageing). By further increasing the polydispersity (SA4), the system becomes non-glassy – fully decaying, implying that particle have local motion and unrestricted reversible particle rearrangements.

5.4 Summary

In this chapter, the ageing behaviour of colloidal hard sphere glasses was characterised by studying the $t_w$-dependency of the ISF. The ageing behaviour was quantified through the ageing index $\zeta$. In section 5.1 it was shown that to a good approximation, any non-stationarity in the fast process, $f(q, \tau < \tau_m^c)$, lies beneath the experimental noise. The fact that the amplitude $A(q)$ agrees with the non-ergodicity factor, $f(q, \infty)$ confirms the validity of the assumption inherent in the PvM method: the existence of a fast process, $f(q, \tau < \tau_m^c)$, quantified through the constant component of the density fluctuations associated with local motions of the particles around fixed average positions, valid for approximately $\tau < \tau_m^c$. This average structure, quantified through the non-ergodicity factor, does not show any significant change as the sample ages. This result is consistent with recent observations from confocal microscopy experiments [47], where only weak correlation is observed between ageing dynamics and structure.

It was also shown, for $\phi > \phi_g$, that the long time decay of the ISF exposes the glass’s non-stationarity. The ideal “aged” glass, defined when $\nu_c(q)=0$, is approached in an algebraic manner. Moreover, in section 5.2 it was shown that the ageing processes, characterised by the ageing exponent $\zeta$, were the same regardless of volume fraction, and were the same for different particle suspensions, suggesting a universality.

It is apparent, from Figure 5.1, and better illustrated in Figure 5.8, that the waiting time dependence of $f(q, \tau)$ increases as delay time increases; it is most pronounced at $\tau = \tau_{max}$ (filled symbols), but almost imperceptible at the crossover (open symbols), $\tau = \tau_m^c$, from the fast process to the slow-ageing process. The crossover between fast and slow processes was quantified in three ways: via (i) the plateau height $f(q, \tau_m^c)$; (ii) the stretching index $\nu_c(q)$; and (iii) the delay time $\tau_m^c(q)$. To illustrate the ageing of the crossover, Figure 5.27 shows the ISF at early and long waiting times for one q vector, and this is shown on an expanded scale.
in the inset: (i) the plateau height $f(q, \tau_m^c)$ agrees with the non-ergodicity factor $f(q, \infty)$ and exhibits almost no ageing behaviour (i.e., the height of the inflection point increases by an almost insignificant amount); (ii) the stretching index $\nu_c(q)$ becomes smaller (the slope decreases), and follows a power law decay with $t_w$. The fact that $\nu_c(q)$ is positive indicates that there is a coupling between the fast and slow processes, and this coupling remains until the end of our experimental time window; (iii) finally, the delay time at which the inflection point occurs increases with waiting time, before apparently reaching stationarity, in the present time window, at long times.

Figure 5.27: Ageing behaviour at the crossover between fast and slow processes for $qR=3.57$.

The results presented in section 5.2, using several volume fractions and a different particle suspension, confirm these results. First, the ISF approaches the non-ergodicity factor algebraically at all delay times $\tau > \tau_m^c$. Second, the non-ergodicity factor $f(q, \infty)$ agrees with $f(q, \tau_m^c)$ and does not show significant $t_w$-dependency, suggesting that no structural changes, on average, occur as the sample ages. Third, the ageing index $\zeta$ does not show significant variation with either scattering vector or volume fraction.

In section 5.3 it was shown for two component systems there was a clear effect of adding the second component – it affected the ageing indices, and it appeared that the bimodal system was not ageing towards an “ideal” glassy state as was the case for the single component
system. These results confirm previous observations of the melting of a glass by the addition of a second component (at constant volume fraction) [102].

Strong interest has been shown in rheological measurements of hard sphere glasses [140-142]. However, as these experiments typically last several thousands seconds, aging occurs during the measurements. As Pham et al. [142] commented, ageing should play a significant role in interpreting rheological data, and measurements such as the ones reported here should be helpful in the interpretation of future rheological measurements.

5.5 Interpretation

Given that the non-ergodicity factor is essentially stationary, Figure 5.27 notwithstanding, the ageing does not affect the (average) structure. This suggests that the only way for the ISF to decay below its non-ergodicity factor is through the exchange of particles: if the slow process is caused by particle exchange, then the process would be stationary if these exchanges were reversible - this would be the case if the particles were all identical. However, in colloidal samples there is always inherent polydispersity – the ageing observed here might be due to the exchange of particles of different size - exchanges which are irreversible, and become rarer and rarer as the sample ages, manifested by the power law ageing behaviour.

Thus we identify a possible mechanism responsible of the ageing or non-stationary behaviour of the slow process – irreversible exchange of particles. The strength of the mechanisms responsible for the ageing behaviour can be reliably quantified by the ageing index $\zeta$, which shows very little $q$ dependence. This applies to samples with relatively low polydispersity (<10%). Upon adding a second component (increasing the polydispersity), the ageing process disappears and the system becomes stationary – ie, particle rearrangements become reversible. This suggests a percolation of the system by the smaller particles.

We close with a conjecture about ageing in terms of the mechanisms by which thermal energy is dissipated. For a system in thermodynamic equilibrium, hydrodynamics dictates that the thermal energy is dissipated via propagating and diffusing momentum currents - sound and flow, respectively. However, to the extent that viscous flow is suppressed in the glass, the thermal energy can only dissipate through propagating momentum currents. In a crystal, propagating modes can be longitudinal and transverse, the latter being allowed due to the presence of lattice planes. To the extent that the glass is amorphous, the thermal energy can only dissipate through longitudinal propagating momentum currents. The latter can stabilize
any force chains of particles, as pictured for example in [143], that may be present. Undissipated thermal energy can create stresses with directions other than that of the force chains. The material may (locally) restructure through collapse of these force chains leading to irreversible events – fracture or local slips – causing non-stationarity or ageing. Such events become rarer and rarer as the sample ages, and are the cause of the observed power law behaviour. It appears, from the stationary behaviour of the non-ergodicity factor, $f(q, \infty)$, at least in the vicinity of the structure factor peak, that the (average) spatial configuration is not affected by these irreversible events. Thus the latter may have a length scale far greater than the distance between neighbouring particles. This is not inconsistent with observed ageing of the non-ergodicity factor of laponite glass at small $q$ [89].

That these irreversible events are strongly affected by the presence of smaller particles indicate that the fracture or local slips occur preferably between particles with different size. The restoration of ergodicity – full decay of the ISF – at high polydispersity for volume fractions which would be a glass at lower polydispersity, is an indication that some of the thermal energy dissipate through (reversible) fracture or local slip events.
Chapter 6. Conclusions

This thesis reported on two major experimental explorations: (i) A study of the effects of volume fraction on the collective dynamics for volume fractions ranging from a dilute suspension, \( \phi = 0.01 \), through to deep in the glass region \( \phi = 0.60 \); and (ii) a study of ageing processes in hard sphere glasses. The conclusions from each of these studies will be considered in turn.

6.1 Effect of volume fraction on collective dynamics

The coherent ISFs measured are consistent with previous observations \([43, 46, 58, 130]\), exposing a slowing of the dynamics as the volume fraction is increased until dynamical arrest is observed at \( \phi_g \) within the experimental time window. However, improvements in experimental procedures, along with newly developed analyses, yielded significant advances in our understanding of the glass transition. The new analysis allowed the characterisation of the \( q \) and \( \phi \)-dependency of non-Fickian processes in terms of: (i) the non-Fickian index \( c_q(q) \); (ii) the delay time \( \tau_m(q) \) necessary for number density fluctuations of spatial frequency \( q \) to forget the effects of packing constraints; and (iii) the current-current correlation function (CCCF). In addition, by drawing on previous measurement of the self ISF, it was possible to express the collective dynamics (number density fluctuations) in terms of the single particle motion (mean-squared displacement), by calculating the mean-squared distance particles must traverse in order for the number density fluctuations of spatial frequency \( q \) to lose memory of packing constraints: \( \langle \Delta r^2(\tau_m(q)) \rangle \).

This analysis led to a number of observations and inferences. First, the saturation of \( \langle \Delta r^2(\tau_m(q)) \rangle \) for \( \phi > \phi_f \), exposes the presence of structural impediments that interrupt or frustrate the decay of density fluctuations of wavevector \( q_m \). These structural impediments – regions of relatively immobilised particles – are associated with dynamical heterogeneities, and expose an impediment to viscous flow on the length scale of the inter-particle distance. Second, the emergence of a negative algebraic decay of the CCCF at \( \phi_f \), similar to that found for the velocity autocorrelation function (VAF) \([33-37]\) can also be interpreted as being due to the presence of immobilised particles. Importantly, the emergence of these and other signatures of dynamical heterogeneities first become apparent at the freezing point, suggesting that there is an inextricable link between freezing and the glass transition.
It was also found that as the volume fraction increases, the q-dependency of \( c_c(q), \tau_m(q), \text{ the CCF and } \langle \Delta r^2(\tau_m(q)) \rangle \) decreases, i.e. there is a decrease in the number of spatial modes q that are able to dissipate the thermal energy via diffusing momentum currents. This indicates that the structural impediments spread from \( q_m \) to other q values, and in particular to lower q. From this one might infer a growing length scale upon approaching \( \phi_g \), as observed in simulation and experiments [19-27].

At \( \phi_g \), the quantities mentioned above have lost their q-dependency – around the peak there are no spatial modes left that are able to dissipate thermal energy and so respond to viscous flow, i.e. flow is suppressed in the glass. The loss of q-dependence also indicates a decoupling of the temporal component of the dynamics from the structure. This decoupling is one of the key features of cage dynamics as predicted by MCT of the glass transition [41]. The particles, in the idealised perfect glass, are caged permanently by their neighbours, in which case the indices \( c_c(q) \) and \( c_s \) should both be equal to one. However, it was shown this is not the case, with both \( c_c(q) \) and \( c_s \) having finite values less than one. This difference could be indicative of some ergodicity restoring processes omitted by the idealised MCT theory. The q-dependence of \( c_c(q) \) indicates that the efficacy of the ergodicity restoring processes is strongest around \( q_m \) – the system attempts to restore ergodicity through (local) rearrangements that must ultimately lead to structures that support lattice modes.

So in summary, partial arrest of number density fluctuations begins to emerge at the freezing point. As the volume fraction is increased, this arrest spreads from the position of the main structure factor peak to other wavevectors. At the same time, the resistance to flow increases, not just because density fluctuations become slower, as for a system in thermodynamic equilibrium, but also because of a decrease in the number of spatial modes by which thermal energy can dissipate. The thermal energy that remains undissipated drives activated processes that must eventually lead to separation of the (equilibrium) crystal phase.

### 6.2 Ageing in colloidal glasses

For \( \phi > \phi_g \), ageing behaviour is observed, indicative of the appearance of irreversible processes. It was found that one-component hard sphere glasses approach an “ideal” glass in an algebraic fashion. This “ideal” glass is one in which all particles are permanently caged
and no (local) particle rearrangement are allowed. These processes appear to be independent of volume fraction (for $\phi>\phi_g$), and independent of the particle suspension studied. It was found that the strength of the mechanisms responsible for the ageing behaviour can be quantified by the ageing index $\zeta$, which shows very little $q$ dependence. It was found that the addition of a second component of smaller size dramatically changes the ageing scenario and, eventually, melts the glass by restoring ergodicity. The latter point confirms previous results [102].

This study also confirmed the assumptions inherent in the PvM method – that in the glass the fluctuations can be decomposed into a constant component (associated with local motions of particles around fixed average positions) and a fluctuating component. The constant component (manifested by the non-ergodicity factor) does not exhibit any ageing behaviour, confirming that dynamical ageing is decoupled from the average structure. In this, the results are in contrast to studies of other soft solids, which appear to show a link between ageing and structure [62, 89]. Using these results, we identified a possible mechanism responsible for ageing in hard sphere colloidal glasses – the irreversible exchange of particles which does not affect the average structure.

### 6.3 Suggestions for future work

The techniques developed in this thesis could be usefully applied to other systems. For hard spheres, it would be worthwhile to conduct a systematic study of polydispersity on the dynamical parameters studied in this thesis. Measuring the partial ISFs for both components of a binary mixture would also yield additional information. Questions that could be posed include: Does an increase of polydispersity suppress the divergence of the relaxation time? Does the melting of the glass observed at high polydispersity (thus restoring ergodicity), also restore viscous flow – ie does it restore the $q$-dependency?

Another avenue to pursue is the study of ageing in attractive hard sphere systems. As found by Pham et al. [80], attractive glasses exhibit stronger ageing behaviour than repulsive glasses. An extensive study of the ageing of attractive glasses remains to be done, and the techniques and analysis used here would help to gain new insights into the nature of glassy dynamics.
As mentioned in Chapter 5, the stationary behaviour observed in the non-ergodicity factor contrasts with other systems, for example Laponite glass [89]. The initial explanation for these differences is that the latter experiments were performed at lower $qR$ than the experiments in the present work. It would be interesting to attempt to measure the non-ergodicity factors for hard spheres at lower $qR$ values to directly compare these results.

The experiments done in chapter 4 were performed at fixed scattering vectors around the structure factor peak. As the peak of the structure factor shifts with volume fraction, most of these measurements are not exactly at the peak. It would be interesting to perform similar experiments corresponding to the exact peak of the structure factor for all volume fractions.

Finally, a complement to the results presented here would be the determination of the linear viscoelastic moduli. Both the storage and loss moduli can be determined using the method of Mason and Weitz [144] [This idea was suggested by D. Weitz at the UCGP conference in Kyoto, Japan 2008]. This was done by numerically calculating the Laplace transform of the measured mean-squared displacement obtained via diffusing-wave spectroscopy (DWS) for colloidal hard sphere particles near the glass transition. A similar analysis could be carried out on the data in this thesis. For volume fractions below the glass this could be done on the self ISF data. For volume fractions above the glass transition, the self ISF and coherent ISF are observed to converge, meaning that this analysis could be carried out on the coherent ISF, with significantly improved accuracy. As (structural) impediments to viscous flow are found to begin at $\phi_c$, from the results of this thesis, it would be interesting to see if such behaviour is also observed in the storage and loss moduli.
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