Chapter 5

Dynamic structure of the non-equilibrium phase

5.1 Introduction

Through the study of temporal speckle fluctuations one can obtain a direct measure of the dynamic properties of a colloidal suspension, a technique known as dynamic light scattering (DLS) (see chapter 3). In this chapter I present results of a DLS study of the non-equilibrium aggregates. Comparison is also made with the static results obtained in the previous chapter. The dynamics of concentrated colloidal suspensions have been studied in detail [53], [135], yet the dynamics of colloidal aggregates and particle gels have remained relatively uninvestigated, as have the dynamics of colloid-polymer mixtures.

5.2 Experimental setup

To conduct these experiments a conventional DLS apparatus was used as shown schematically in figure 5.1. The system comprises an Ar$^+$ laser ($\lambda = 514.5\, nm$), with a focused beam, passing through a cylindrical water bath which was regularly filtered to remove
dust. The sample is contained in a cell of cross section $1cm \times 1cm$, and is positioned in the centre of the water bath. In this setup refraction at the cell-water interface must always be taken into account when calculating the resulting scattering vector. The light scattered at an angle $\theta$ is focused onto a slit, which passes to an aperture in front of the PMTs, normally adjusted to the size of a single coherence area (speckle). The light then enters a beam splitter and into two separate PMTs, positioned perpendicular to one another. The two signals form the input to a Photon correlator (ALV-5000) controlled by a PC. The PMTs can be rotated on a goniometer to study different $Q$ vectors and therefore the dynamics of the suspension on different length scales. Finally the whole system is floated on a steel table to remove the effect of vibrations.

Such a setup is ideal for studying ergodic samples. If one studies non-ergodic samples, i.e. samples with density fluctuations which relax on a time scale far greater than that of the experiment, then a different setup must be utilised in order to obtain a fully ensemble averaged field correlation function. In this study the improved manual
case was used (as defined in section 3.5.3) so that ten different speckles were measured simultaneously. To do so one first inserts an ergodic sample into the apparatus and the optics adjusted until the intensity correlation function has an intercept of 2 i.e. approximately one coherence area is measured (see section 3.5). The initial focusing lens is removed and the aperture opened until the intercept drops to approximately 1.1 i.e. the coherence is decreased by a factor of ten, and one can then assume that approximately ten independent Fourier components are measured at once. In doing so one can introduce stray light so care must be taken to shield the PMTs. A number of measurements can then be taken of the non-ergodic sample and the results combined to obtain a full ensemble average. In practice one must take an increasing number of measurements until iteratively one obtains reproducible correlation functions.

The output signals from the PMTs were cross-correlated throughout to remove the effect of after-pulsing. After-pulsing is observed if residual gas atoms are present in a PMT, which occurs if the vacuum leaks over time. If the primary electron has sufficient energy to ionize a residual gas atom then the ion becomes highly attracted to the primary photo-plate. The ion strikes the plate and another electron is emitted, resulting in two pulses, one primary one secondary, in the PMT signal. In conventional light scattering this has no overall effect as one extra count in several thousand is negligible, yet in DLS one finds a correlation between these two pulses. It is highly unlikely that this should occur in two PMTs at the same time (probability $\sim 10^{-6}$) and therefore by cross-correlating the signals one removes the spurious correlation. After-pulsing occurs on a very short time scale and tends to distort the initial short-time decay of the intensity correlation function.

Thermal lensing [136] was found to be a considerable problem for samples near index match, especially using the $Ar^+$ laser. Thermal lensing occurs when the incident laser intensity heats the sample. In doing so a temperature gradient is set up which induces convective flow and acts to expand the beam like a lens. Thermal lensing was easily identified, as the straight through beam became greatly expanded and the shape
of the intensity correlation function indicated an extremely fast short-time diffusion. To remove this problem the Ar$^+$ laser could be replaced by a low power He-Ne laser, $\lambda = 632.8 \text{ nm}$, which although appeared to remove thermal lensing, led to problems in signal detection as the sample only scattered weakly.

A detailed discussion of DLS techniques can be found in reference [136].

5.3 Temporal evolution of the single particle dynamics

Sample 9 (see the $\phi \sim 0.1$ section of table 4.1) was taken as a typical example of a sample in the transient-gelation regime of the non-equilibrium region and the single particle dynamics were measured as the structure grew, became arrested and then collapsed. Care had to be taken to avoid measurements at the minimum of the form
factor, as these would only probe the effects of polydispersity [92]. Therefore the minimum was always estimated by eye before the appropriate wavevector to study was chosen. Measurements were taken using the apparatus shown in figure 5.1 at a scattering wavevector $Qa \sim 6.25$. As the main peak in the non-equilibrium structure factor occurs at $Qa \sim 3.9$ one can assume that only single particle motion is studied at such a high $Q$ vector, and one simply measures a self diffusion. It is well known that the effect of non-ergodicity is small at high wavevectors [88], i.e. as on such short length scales the particles do not feel the presence of the frozen-in structure, and accordingly the correlation functions and first channels at $Qa \sim 6.25$ were found to be highly reproducible when a single measurement was performed with an expanded aperture, i.e. ten speckles (individual Fourier components) were sufficient to obtain the full ensemble average. Two such ensemble averaged correlation functions are shown in figure 5.2 for a typical transient-gelation type sample, in its arrested state.

Sample 9 was tumbled thoroughly, inserted into the apparatus and consecutive intensity correlation functions measured until visible sedimentation was observed. Each measurement was of duration 500 seconds. The resulting intensity correlation functions were then converted into normalised field correlation functions using equation (3.36), and are shown in figure 5.3 in both the linear-log and log-linear representations. For non-interacting Brownian particles the correlation function would be a single exponential (c.f. equation (3.49)) and simply a straight line in the lower figure.

Obviously the field correlation functions are far from single-exponential [18] i.e. as expected these are highly-interacting systems. In fact the correlation functions take on the form of stretched exponentials,

$$g^{(1)}(Q, \tau) \sim e^{-(\tau/\tau_c)^b}$$  \hspace{1cm} (5.1)

where $\tau_c$ is a characteristic time and $0 < b < 1$. Such a correlation function
Figure 5.3. Field correlation functions as a function of delay time for sample 9. Circles ≡ the first, Squares ≡ the second, Triangles ≡ the third, Diamonds ≡ the fourth, Pentagram ≡ the fifth Crosses(+) ≡ the sixth, Crosses (×) ≡ the seventh and Asterisks ≡ the eighth 500 seconds.
Figure 5.4. (a) The structural relaxation time as a function of time for sample 9. (b) The small angle peak position against time for sample 9.
would suggest decay processes which relax over many similar time scales, rather than a single characteristic time. The correlation functions never decay as single power laws which were observed by Martin et al. [137], [138] in silica gels. They attributed such behaviour to long range fractal structure and self similar relaxation times, although without taking non ergodicity into account the validity of their data is questionable. Analogies can also be drawn between the non-equilibrium behaviour and the colloidal glass transition, found at high colloid volume fraction in the absence of polymer [89], [139] - [141]. In this case particle motion becomes retarded as the particles become caged-in by the presence of all the others, due to the very high volume fraction of the suspension, rather than through an attractive potential. Close to the glass transition the field correlation functions show two independent decay processes: the $\alpha$ decay associated with the final breakdown of particle cages and the $\beta$ decay associated with the slow rearrangements of the particle cages. In the colloid-polymer non-equilibrium aggregates there appears to be no evidence for the $\beta$ decay, perhaps due to the processes relaxing on similar time scales so that the $\alpha$ and $\beta$ decays become superimposed.

Note also the large amount of statistical noise in the correlation functions at long times. To improve this data one would require extremely long runs which would then encompass the growth, arrest and collapse of the structure. Therefore there is an obvious trade-off between a long experimental time to obtain good statistics against a shorter experimental time to avoid integrating over too many different dynamic regimes.

One possible way of characterising these stretched exponential decays is to measure the structural relaxation time, i.e. the time taken for the field correlation function to decay to $\left(\frac{1}{e}\right)$ of its initial value. In the high-$Q$ limit (yet less than $Q \to \infty$) the structural relaxation time corresponds to the time taken for a particle to diffuse a distance comparable to its own diameter. Without a long-time single-exponential decay it becomes impossible to measure a long-time diffusion coefficient, so the structural relaxation time would appear the most appropriate measure of the long-time diffusion. The structural relaxation time as a function of elapsed time is shown in figure 5.4(a).
Below is the small angle peak position plotted against the same time axis, data which was shown previously in figure 4.14.

The relaxation time shows a marked increase as the small angle ring collapses and freezes i.e. the single particle diffusion slows down as the large scale structure becomes arrested. As the small angle ring fills in completely the relaxation time suddenly decreases (after approximately 2000 seconds) and does so until visible sedimentation is observed. Although it is reassuring to observe particle motion consistent with the small angle scattering data, the comparison is limited as each correlation function represents an integration over 500 seconds and one loses time resolution i.e. the afore-mentioned trade-off. Interestingly as the small angle ring remains stationary the structural relaxation time still increases (100 < t < 2000), and one can conjecture that the structure is compacting over this period, as indicated by the reduction in the long time diffusion. Meanwhile the large scale structure remains unaffected as the short length-scale structure evolves. As the large length scale structure collapses, i.e. when the small angle ring fills-in, the single particle motion rapidly increases.

Even when the large scale structure is in a completely arrested state i.e. the persistence of a frozen ring, the correlation functions still decay, albeit slowly, indicative of slow single particle motion, which as above, one could conjecture acts to compactify the local small scale structure. As the depletion potential depth is only a few $k_BT$ any small thermal fluctuations will be sufficient to break the interparticle bonds and the structure will tend to compact locally as bonds break and reform, until the structure no longer percolates and the now discrete clusters settle under gravity.

What should also be noted from figure 5.3 is the time-invariant, short-time limit of the correlation function, $0.92 \lesssim g^{(1)}(Q, \tau) < 1$. This would suggest that the very short-time motion is insensitive to the large scale structure.
5.4 Short-Time dynamics

In a typical non-equilibrium sample each particle will sit in the depletion potential surrounded by its nearest neighbours in the aggregate. In the very short-time regime the particle diffusion is simply governed by its hydrodynamic interactions with the surrounding particles. As each particle has a typical thermal energy of $k_BT$ the short-time motion, on a slightly longer time scale, should be governed by the particles 'rattling' about some mean position, at a range given by the width of the depletion potential $k_BT$ above its minimum. As the bonds are only a few $k_BT$ in depth, small thermal fluctuations will then break the bond and the particle will diffuse throughout the sample. Thermal vibration of particles about their equilibrium positions is consistent with a Debye-Waller like motion (DWM) [142] in atomic systems. Such motion would be insensitive to the large scale structure, consistent with that observed in figure 5.3.

To test this hypothesis the short-time motion of a number of samples was examined. So far the polymer has been largely ignored and all theoretical interpretations have assumed a simple one-component colloidal suspension subject to a strong, short-ranged attractive potential. When the short-time motion is studied care must be taken to account for the polymer diffusion which would contribute to these short-time scales, as the polymer free diffusion is 14 times faster than that of the colloidal particles. Similarly any slight differences in solution viscosity between samples with more or less added polymer has so far been ignored.

To account for the polymer scattering the samples were first centrifuged until all the colloidal particles were contained in the sediment. Then the correlation function of the polymer solution in the supernatant was measured. Assuming that the overall correlation function is simply a linear superposition of the individual colloid and polymer correlation functions scaled by their relative intensities, one can write,
\[ g^{(1)}(Q, \tau)_{\text{colloid}} \sim \left( \frac{1}{1 - \chi(Q)} \right) g^{(1)}(Q, \tau)_{\text{total}} - \left( \frac{\chi(Q)}{1 - \chi(Q)} \right) g^{(1)}(Q, \tau)_{\text{polymer}} \] (5.2)

where \( \chi(Q) \) is the ratio of polymer to colloid scattering, \( \chi(Q) = I_{\text{pol}}(Q)/I_{\text{col}}(Q) \). As \( \chi(Q) \) is small (of the order of 4%) and as the polymer correlation function decays quickly the overall correction will be small, yet must still be taken into account. Samples were also prepared with appropriate concentrations of polymer and a few trace colloidal particles of known size. By measuring the short-time diffusion coefficient of the colloidal particles one can infer the viscosity of the background solution \( \eta \) through the Stokes-Einstein equation. Surprisingly the correlation functions did not decay as single exponentials despite the dilute nature of the suspension. This phenomenon is as yet poorly understood. In each case only the short-time motion of the colloidal particles was measured to obtain a diffusion coefficient and infer the background viscosity.

Field correlation functions were measured for a number of non-equilibrium samples at \( Qa \sim 6.25 \), details of which are given in table 5.1. Using equation (3.55), and assuming self diffusion, mean squared (MS) displacements of the particles were calculated from each sample in its most arrested state. These are shown in figure 5.5 against a time scaled by the relative viscosities of the polymer solutions \( \left( \frac{\eta_a}{\eta} \right) \). It must be stressed that the correction for the polymer scattering is negligible on this long time scale \( \tau > 1 \times 10^{-4} \text{ secs} \). As is evident one can define two regimes within the MS displacement, one short-time and one long, as the displacement tends to saturate at long times. It is somewhat arbitrary as to how one defines ‘short’ or ‘long’. The distinction was made at the point where the diffusion coefficient had decayed to one hundredth of its initial value and by extrapolating back one can estimate a range for the short-time motion. Below in figure 5.5 is the root mean squared short-time motion for each of the samples, against the range of the depletion potential, \( k_BT \) above its minimum.
Figure 5.5. Mean squared displacements, Circles ≡ sample 25, Squares ≡ sample 26, Diamonds ≡ sample 9 and Triangles ≡ sample 24. Below is the root mean squared displacement against the predicted short-time motion.
<table>
<thead>
<tr>
<th></th>
<th>$\phi$</th>
<th>$C_P$</th>
<th>$\xi$</th>
<th>predicted DWM</th>
<th>measured short-time motion</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>0.100</td>
<td>6.27e-3</td>
<td>$\sim 0.07$</td>
<td>$5.0 \text{ nm}$</td>
<td>$9.7 \pm 0.4 \text{nm}$</td>
</tr>
<tr>
<td>24</td>
<td>0.198</td>
<td>3.91e-3</td>
<td>$\sim 0.07$</td>
<td>$5.2 \text{ nm}$</td>
<td>$9.1 \pm 0.4 \text{nm}$</td>
</tr>
<tr>
<td>25</td>
<td>0.212</td>
<td>3.35e-3</td>
<td>$\sim 0.07$</td>
<td>$6.2 \text{ nm}$</td>
<td>$10.0 \pm 0.4 \text{nm}$</td>
</tr>
<tr>
<td>26</td>
<td>0.192</td>
<td>2.74e-3</td>
<td>$\sim 0.19$</td>
<td>$18.1 \text{ nm}$</td>
<td>$14.5 \pm 0.4 \text{nm}$</td>
</tr>
</tbody>
</table>

Table 5.1. Various non-equilibrium samples alongside their predicted DWM and measured root mean squared short-time motion.

Within error the data is certainly consistent with a short-time Debye-Waller type motion. As shown in figure 5.3 this motion persists throughout the growth and collapse of the large-scale structure. As one expects the short-range structure to remain roughly constant throughout, i.e. the particles remaining in close proximity to one another, it comes as no surprise that the short length scale Debye-Waller motion is time invariant.

Rather than simply studying the self motion, at high-$Q$, it would now appear appropriate to study the $Q$-dependence of the short-time dynamics and therefore the dynamics over a wide range of length scales.

### 5.5 $Q$-dependent dynamics

The dynamics of structured suspensions are known to be highly $Q$-dependent [53]. Sample 12 was chosen as a typical example of a non-equilibrium sample which underwent transient-gelation, i.e. a highly structured state, and the $Q$-dependence of the dynamics was examined in its most arrested state.

The sample was homogeneously mixed and a correlation function taken after approximately 500 seconds, to observe the slowest, arrested, motion (c.f. figure 4.15. Such motion is equivalent to that measured at 2000 seconds from sample 9, shown in figure 5.4(a)). With an enlarged pin hole a 500 second run was taken and ten independent Fourier components measured. At low wavevectors non-reproducible correlation
functions, highly fluctuating intensities and low first channels were observed i.e. fingerprints of non-ergodicity. Therefore a number of correlation functions were measured until reproducible ensemble averages were obtained. It was found that by repeating the same procedure ten times, and constructing an ensemble average encompassing 100 independent speckles, one obtained highly reproducible correlation functions. As shown in figure 5.6 the reproducibility of the ensemble averaged correlation functions was found to be excellent, until very late stage when the so called ‘non-ergodic background’ was found to have a statistical error of ±10%. Such an error in the long time decay of the correlation function is typical [143]. The non-ergodic background, i.e. that the correlation function does not decay to zero, is indicative of the presence of frozen-in density fluctuations. The density fluctuations on this length scale relax on a time scale far greater than that of the experiment. As sample 12 was within the transient gelation
regime, the observation of frozen-in density fluctuations is consistent with the arrested structure suggested by the small angle scattering shown in figure 4.15.

These ensemble averaged correlation functions were measured from sample 12, over a wide range of wavevectors \((2 < Qa < 7)\), and the full \(Q\)-dependent short-time diffusion coefficient measured. Again at these short time scales the polymer scattering had to be accounted for and in fact the short-time diffusion coefficient was found to be rather sensitive to the polymer scattering. Also care had to be taken when measuring the short-time diffusion coefficient as the correlation functions were highly non-single exponential. The short-time decay of the correlation functions were fitted to linear, quadratic and cubic polynomials, and by fitting over shorter and shorter regions a number of diffusion coefficients were measured using equation (3.51). The diffusion coefficients obtained from each of the polynomials converged as the fitting
region decreased. At the same time the statistical uncertainty grew as less data was used in the fitting procedure, which caused the data to diverge. Therefore from the behaviour over large fitting regions one can then extrapolate back to obtain an effective short-time diffusion coefficient. A typical example of the fitting procedure is shown in figure 5.7. A similar technique was used by Brown et al. [144] who studied non-exponential relaxations of polystyrene in cyclohexane.

As shown in figure 5.8(a) the short-time diffusion coefficient obtained by this method varies inversely as the static structure factor (see figure 4.45), consistent with equation (3.52). After measuring the experimental structure factor, equation (3.52) can be used to calculate the full $Q$-dependent hydrodynamic factor (or mobility) as shown in figure 5.8(b). The solid line represents the hydrodynamic factor of a hard-sphere fluid of volume fraction $\phi = 0.2$ calculated from the theory of Beenakker and Mazur [86], [87], using a code provided by D.J. Pine. Strikingly the measured hydrodynamic factor is far reduced, compared to that of a hard-sphere fluid. This implies that the particles interact strongly through a hydrodynamic coupling, due to their close proximity to other particles in the aggregate. The reduction in the hydrodynamic factor can be attributed to a large increase in the local volume fraction. If one compares the high-$Q$ limit (i.e. short-time self diffusion $D_s$) with the theory of Beenakker and Mazur (only really valid up to $\phi \sim 0.3$) one can infer a local volume fraction of particles $\phi_L \sim 0.58$, which compares well with that obtained by microscopy in section 4.4.4. Note also the shift in the peak of the hydrodynamic factor to larger wavevectors, due to the small interparticle separation i.e. the hydrodynamic factor has a peak coincident with the peak in the static structure factor, consistent with that seen in simple hard-sphere fluids [53], [86], [87], [135].

Again to characterise the long-time decays of these correlation functions one can measure the structural relaxation time. Figure 5.9 shows the $Q$-dependent structural relaxation time measured from sample 12, multiplied by the square of the appropriate wavevector. To compare decays at different wavevectors one must obviously take into
Figure 5.8. (a) The free diffusion coefficient $D_0$ divided by the effective short-time diffusion coefficient $D_{eff}(Q)$ for sample 12. (b) The hydrodynamic factor $H(Q)$ of sample 12. The solid line represents the theory of Beenaker and Mazur for a volume fraction $\phi = 0.2$, calculated using a code provided by D.J. Pine.
account the $Q^2$-dependence of the diffusion coefficient (c.f. equation (3.51)). The structural relaxation time, in accord with the short-time dynamics presented above, varies inversely as the static structure factor. In hard-sphere suspensions it is known that the long-time diffusion coefficient varies inversely as the static structure factor [135]. In this case a long-time diffusion coefficient can be measured as the long-time decay of the field correlation function follows a single exponential. Although in the case presented here one cannot measure a long time diffusion coefficient, due to the highly stretched exponential nature of the correlation functions, it is reassuring that a property of the long-time diffusion, the structural relaxation time, varies in a similar manner.

5.6 Long-time dynamics
Table 5.2. Samples all of volume fraction $\phi \sim 0.2$ and increasing in polymer concentration.

<table>
<thead>
<tr>
<th></th>
<th>$\phi$</th>
<th>$C_p$</th>
<th>Phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>0.182</td>
<td>0</td>
<td>Fluid</td>
</tr>
<tr>
<td>b</td>
<td>0.202</td>
<td>2.18e-3</td>
<td>Fluid</td>
</tr>
<tr>
<td>c</td>
<td>0.203</td>
<td>2.46e-3</td>
<td>Fluid</td>
</tr>
<tr>
<td>d</td>
<td>0.203</td>
<td>2.70e-3</td>
<td>Fluid</td>
</tr>
<tr>
<td>e</td>
<td>0.200</td>
<td>2.80e-3</td>
<td>Fluid</td>
</tr>
<tr>
<td>f</td>
<td>0.202</td>
<td>3.06e-3</td>
<td>Fluid-Crystal</td>
</tr>
<tr>
<td>g</td>
<td>0.203</td>
<td>3.24e-3</td>
<td>Non-equilibrium</td>
</tr>
<tr>
<td>h</td>
<td>0.201</td>
<td>3.46e-3</td>
<td>Non-equilibrium</td>
</tr>
<tr>
<td>i</td>
<td>0.202</td>
<td>3.66e-3</td>
<td>Non-equilibrium</td>
</tr>
<tr>
<td>j</td>
<td>0.202</td>
<td>3.88e-3</td>
<td>Non-equilibrium</td>
</tr>
</tbody>
</table>

It was shown that a sample within the transient-gelation regime of the non-equilibrium region exhibits frozen-in density fluctuations at very long time scales. To examine the long-time dynamics, and its dependence upon different regions of the phase diagram, a number of different samples were prepared of volume fraction $\phi \sim 0.2$ and varying in polymer concentration, given by table 5.2. These ranged from single phase fluids (samples a to e), to a fluid-crystal coexistence sample (sample f) and four different non-equilibrium samples (samples g to j). The non-equilibrium samples spanned the spinodal-like (sample g) and transient-gelation regimes (samples h to j). Full ensemble averaged measurements were only necessary for the non-equilibrium samples, as the other samples showed highly reproducible correlation functions i.e. these represented fully ergodic systems. Three measurements were carried out at wavevectors $Qa = 2.5$, $Qa = 3.3$ and $Qa = 5.5$ i.e. one well below, one near, and one well above the main high-$Q$ peak in the structure factor. To compare the non-equilibrium samples directly, they were all homogeneously mixed and correlation functions taken 500 seconds later, each of duration 500 seconds. The resulting normalised, ensemble averaged, field correlation functions are shown in figures 5.10(a), 5.10(b) and 5.11. It was latterly found that the short-time decays of the correlation functions contained the effects of after-pulsing as only one PMT was used in this study. Accordingly the data at very short-times is
Figure 5.10. (a) Correlation functions taken at $Qa = 2.5$. (b) Correlation functions taken at $Qa = 3.3$. Fluid samples, Circles (empty) $\equiv a$, Squares $\equiv b$, Triangles $\equiv c$, Diamonds $\equiv d$, Pentagons (empty) $\equiv e$. Coexistence sample, Crosses (+) $\equiv f$. Non-equilibrium samples, Crosses ($\times$) $\equiv g$, Asterisks $\equiv h$, Pentagons (filled) $\equiv i$ and Circles (filled) $\equiv j$. 
Figure 5.11. Correlation functions taken at $Qa = 5.5$. Fluid samples, Circles (empty) $\equiv a$, Squares $\equiv b$, Triangles $\equiv c$, Diamonds $\equiv d$, Pentangles (empty) $\equiv e$. Coexistence sample, Crosses ($i$) $\equiv f$. Non-equilibrium samples, Crosses ($\times$) $\equiv g$, Asterisks $\equiv h$, Pentangles (filled) $\equiv i$ and Circles (filled) $\equiv j$.

unreliable and will not be discussed further.

The hard-sphere fluid (sample $a$) shows a fast, single exponential decay at all three wavevectors. As the polymer concentration is increased little happens to the field correlation function, so long as the increase in background viscosity is accounted for. The correlation functions all deviate from single exponential decays and have similar relaxation times. Once the phase boundary is crossed the sample which ultimately crystallises shows a marked decrease in the particle dynamics, and again a deviation from single-exponentiality. Once into the non-equilibrium region the dynamics become progressively arrested, as the polymer concentration is increased. Again one recovers the highly non-exponential decays observed previously. At high wavevectors the non-ergodic background is small. At lower wavevectors a large non-ergodicity is observed
Figure 5.12. $Q$-dependent structural relaxation time as a function of polymer concentration.

for all but the spinodal-like sample (sample $g$), although it must be stressed that the non-ergodic background measured by this method is only accurate to within $\pm 10\%$. Consistent with the arrested large scale structure in the transient-gelation regime, the non-ergodic backgrounds suggest non-decaying density fluctuations, although in contrast to the colloidal glass transition, crystallisation becomes suppressed before the persistence of these frozen-in density fluctuations i.e. within the spinodal-like regime.

To characterise these highly non-exponential decays, one can again measure the structural relaxation time. In figure 5.12 the structural relaxation time is shown as a function of polymer concentration, normalised by the relative background viscosities and multiplied by the square of the appropriate wavevector. As is evident from figure 5.12 little happens to the relaxation time until one enters the non-equilibrium
region, upon which the relaxation time diverges rapidly. In fact the relaxation time divergence is consistent with a power law, yet as this is fitted over such a small region the relevance is somewhat dubious. Concomitant the relaxation time and therefore the dynamics of the system become progressively more $Q$-dependent i.e. the system tends to become highly structured as the state becomes arrested. The spinodal like sample (sample $g$) has very little $Q$-dependence to its relaxation times, consistent with the lack of frozen-in structure and accordingly the absence of a non-ergodic background.

5.7 Concluding remarks

In this chapter I discussed the dynamic structure of the non-equilibrium phase. Although a number of interesting phenomena have been observed a fundamental trade-off limits the information which can be gleaned from such a dynamic measurement: a long experimental time is required for good statistics, whereas a short experimental time improves the time resolution of the measurement as the structure evolves continuously.

Despite this limitation the dynamics have been examined for a number of samples. The single particle dynamics of a typical sample which undergoes transient-gelation has been measured, and the time-dependence of the dynamics is found to be consistent with the previously presented small angle data. Interestingly the short-time motion is found to be invariant to the large scale structure, throughout the systems evolution and appears to be consistent with a Debye-Waller like motion. The $Q$-dependent effective diffusion coefficient associated with this short time motion has been measured and is found to vary inversely as the static structure factor as does the structural relaxation time, consistent with other colloidal systems. Finally a number of samples were studied at a single volume fraction and increasing in polymer concentration. The structural relaxation time was seen to diverge as the non-equilibrium boundary was crossed. It was also found that samples which underwent transient-gelation showed the persistence of frozen-in density fluctuations at long times, whereas spinodal-like samples did not.
Such arrested structure is consistent with that suggested by small angle scattering. Although a significant error exists in the non-ergodic background obtained by this method, it still appears to be the most appropriate for studying weakly flocculated structures (see section 3.5.3).

Little theoretical work has yet been presented on the dynamics of highly interacting systems. As such these systems represent complex many-body problems and in my opinion computer simulation is the most likely route to render these problems soluble. For example lattice Boltzmann simulation of the dynamics of hard-sphere systems has recently been presented, which matches experiment over a wide range of density [135]. This type of simulation could now be extended to model the colloid-polymer system and in particular study the highly non-exponential relaxations observed in the non-equilibrium aggregates.