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Glass transition dynamics of hard sphere like microgel colloids with short-ranged attractions

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Abstract

We have studied by dynamic light scattering the glass transition dynamics of a binary mixture of polystyrene microgel particles with a size ratio of $R_{\mathrm{small}}/R_{\mathrm{large}} = 0.81$ and a number ratio of $N_{\mathrm{small}}/N_{\mathrm{large}} \approx 2.7$, where a short-ranged depletion attraction ($\delta \approx 0.06$) was induced by addition of linear polystyrene. This system shows a reentrant glass transition. We have determined the glass transition lines of this system in the experimental control parameter space given by the colloid volume fraction φ and the polymer concentration c_{p} by employing the power law of mode coupling theory (MCT) for the α-relaxation times. We find a reentry region which is much larger than predicted by theory and reported for another colloidal system with depletion attractions. Analysing the fluid dynamics along the transition lines with the β-scaling law of MCT we extract the c_{p} dependence of the exponent parameter λ and the non-ergodicity parameter f_q^c. The results are in qualitative agreement with the prediction of MCT for increasing attraction strength. The observed 'jump' of f_q^c is indicative of a change of the close by glass phase from a packing-driven to a bonding-driven glass. The increase of λ to 0.91 and its subsequent decrease may indicate the neighbourhood of an A_4 singularity.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Colloidal dispersions have served over the past decades as model systems for addressing fundamental questions of condensed matter science such as crystallization [1, 2], glass formation [3, 4] and gelation [5]. In particular the understanding of the physics of vitrification has been significantly improved by the interplay between the mode coupling theory (MCT) of the glass transition [6] and light scattering experiments on colloidal particles with hard sphere interactions [7, 8]. All major predictions of the theory have been verified by experiment on a 10% error basis for this simplest glass forming system [9], thus establishing the role of MCT as the leading paradigm for the glassy freezing of simple liquids. The theory identifies the so-called cage effect—the transient trapping of particles in cages formed by neighbouring particles—as the dominant mechanism of the dramatic slowing down of structural relaxation on the increasing packing density. Eventually this slowing down leads to a dynamical arrest of the particles when the timescale of their structural relaxation becomes larger than the timescale of the experimental probe—the glass transition occurs. In the neighbourhood of this glass transition the dynamics is ruled by two scaling laws giving rise to power law divergence of two timescales—one, τ_σ, describing the motion of the particles in their respective cages and the other, τ_α, corresponding to the breaking up of the cages and escape of particles from them. As τ_α diverges faster than τ_σ the density correlator, $f(q, \tau)$, describing the particle density fluctuations develops a characteristic two-step decay with the emergence of a plateau which becomes more extended in time with increasing packing density. In the idealized version of MCT, structural relaxation stops at the glass transition and only the cage motion prevails [6]. As a consequence the glass transition is indicated by a discontinuous jump of the long-time limit, $f(q, \infty)$, of the density correlator from zero to a finite value f_q^c, which describes the value of a plateau which now extends to infinite times. In this description the glass transition is a sharp transition from an ergodic to a nonergodic system which takes place at a definite temperature or packing density.

In real glass forming systems there has been, however, always observed a final decay of the density correlator which terminates the plateau. Obviously, there exist dynamical processes that counteract the cage effect by restoring ergodicity, which are not included in the idealized MCT. The nature of these ergodicity restoring processes is not entirely clear—thermally activated (or phonon-assisted hopping) processes [10], crystallization [8, 11] and ageing [12, 13] have been addressed as possible candidates in different contexts. In colloidal dispersions where phonon-assisted hopping is expected to be absent (due to overdamping via the solvent degrees of freedom) and crystallization has been effectively suppressed [14] or significantly slowed down [12] so as to play no role on the timescales relevant for glassy dynamics, nevertheless some final decay of the density correlators or the tagged particles correlators has been observed in glassy samples. Here at least, ageing processes seem to be responsible for the long-time dynamics which lead to deviations from the scenario predicted by the idealized MCT.

Disregarding ageing which affects usually only the dynamics at very long experimental timescales, the idealized MCT has turned out to provide a universal description of the glassy freezing of colloidal particles in the sense that the same scaling laws are found for both short-ranged hard-sphere like [7, 8] and long-ranged Yukawa-like repulsive interactions [15]. The differences in interactions are only reflected in details such as the numerical values of critical exponents and glass transition volume fractions. This also applies for Brownian particles where attractions are present which are long-ranged as compared to the particle diameters, as can be inferred from computer simulations studies of a binary mixture of Lennard-Jones atoms with stochastic short-time dynamics [16, 17].

Recently, however, it has been predicted that the glass transition scenario changes dramatically and that qualitatively new glass physics arises when attractions become very short-ranged [18–21]. Whereas the glass transition of hard spheres is driven by just one control parameter, the packing density (or the volume fraction φ) of the glass transition in the case of short-ranged attraction is now controlled by three parameters—the volume fraction $\varphi = \rho\pi d^3/6$ (where ρ is the particle number density and d the particle diameter), the dimensionless attraction strength $\Gamma = u_0/(k_B T)$ (where u_0 is the depth of the attraction well) and the relative attraction width $\delta = \Delta/d$. Theory predicts that on increasing the attraction strength the glass transition volume fraction should recede to higher values if the attraction range is sufficiently small (e.g. $\delta < 0.1$). Thus the hard sphere glass transition evolves into a glass transition line in the (φ, Γ) plane. At even higher attraction strengths this line bends back again to lower volume fractions and runs more or less parallel to the φ-axis. This behaviour gives rise to a new phenomenon: the reentrant glass transition. By switching on a short-range attraction a hard sphere glass should melt and on further increase of attraction strength it should freeze again, however, into another type of glass. The driving force for glassy freezing should now be the formation of transient bonds which become more and more permanent with increasing attraction until dynamics is arrested again. This new type of glassy state has been termed attractive [22] or bonding-driven [23] glass to distinguish it from the familiar hard sphere glass whose extension into the regime of low attractions strength has been named correspondingly repulsive or packing-driven glass. One major distinction of this new type of glass is the absence of the cage effect and a shift of the plateau to such high values that it becomes difficult to detect experimentally. Due to the distinct natures of the two types of glass one usually speaks of two branches of the glass transition line—a repulsive and an attractive one, which join continuously.

Short-ranged attractions where the attraction range is less than 10% of the particle radius do not exist in atomic or molecular liquids, but they can be realized in colloidal dispersion by the addition of small non-adsorbing polymer [24]. This is achieved by the well-known depletion effect, where the polymer chains are excluded from the space between two colloidal particles at close distance. The resulting misbalance of the osmotic pressure exerted by the polymers acts then as an effective attractive force. The so-called depletion potential has been worked out [25–27], indicating that the attraction strength and the attraction range can be tuned by varying the concentration and the size of the polymer, respectively. This means that increasing the polymer concentration c_p in a colloid–polymer mixture has the same effects as reducing the temperature in an atomic system. Inducing short-ranged attractions into hard sphere-like colloidal dispersions in this manner, the reentrant glass transition and the different characteristics of the bonding driven glass have been verified [14, 23, 28, 29]. In addition, the reentry phenomenon been has found in a number of simulation studies [28, 30–32].

This scenario again changes if the attraction range becomes very short, e.g. $\delta = 0.03$. In this case the repulsive glass transition line stops when it meets the attractive one, while the latter continues and ends in a kind of critical point [21]. In the language of MCT this point is addressed as an A_3 singularity (the repulsive and attractive transition lines are named A_2 singularities). The line between the crossing point and the A_3 singularity is the locus of transition points from packing-driven to bonding-driven glass states. This transition is reflected in a discontinuous jump of the nonergodicity parameter $f(q, \infty)$ [21]. Increasing the attraction range again towards a characteristic value, $\delta \to \delta^* \approx 0.04$, the glass–glass transition line shrinks and the A_3 singularity approaches the crossing point [33]. A special situation arises when the A_3 singularity and the crossing point coincide (at δ^*). This is the locus of another higher-order singularity—an A_4 singularity. Close to these higher-order singularities the glass transition dynamics differ significantly from that of the familiar A_2 scenario. A most prominent feature is the appearance of logarithmic decay laws in different time domains of the density correlators [21]. Such logarithmic decay laws have been observed in simulations studies [34, 35] and experiments [29, 36]. However, it is not in all cases clear if the observed logarithmic decays indicate the proximity of an A_3 or an A_4 singularity, or if they are just a result of the complicated interplay of the different singularities which can lead to apparent logarithmic sections in the density correlators as has been indicated by carefully analysing the dynamics close to the various singularities [37–39]. In addition, it is by no means clear if a simple mapping between experimental and theoretical control parameters, especially between the polymer size and δ, is possible, which would allow to localize the A_3 and A_4 singularities. This has so far only been achieved in a simulation study [35]. In any case such a mapping requires at least the localization of the glass transition lines for one attraction range.

Recently, we have shown for two volume fractions that the phenomenon of reentry exists in a binary mixture of microgel particles with nearly hard sphere-like interactions when depletion attractions are introduced by the addition of a non-adsorbing free polymer. In this contribution we will present and analyse light scattering data in the complete reentry region which allow establishing the location of the glass transition lines. By analysing the lines shape of the density correlator along the transition lines we will address the question of the occurrence and location of higher order singularities in our system.

2. Experimental details

2.1. System characteristics

The studied colloidal dispersion consists of a binary mixture of polystyrene microgel particles with a stoichiometric crosslink density of 1:50 (1 crosslink per 50 monomers; crosslinker: *m*-diisopropenylbenzene) in the good and isorefractive solvent 2-ethylnaphthalene with the size ratio $R_{\mathrm{small}}/R_{\mathrm{large}} = 185\ \mathrm{nm}/150\ \mathrm{nm} = 0.81$ and a number ratio of $N_{\mathrm{small}}/N_{\mathrm{large}} = 2.65$. The intrinsic polydispersity ($\sigma = 0.08$) of the individual components is small enough for crystallization to proceed. This allowed studying the phase behaviour of the individual components from which information about interactions and absolute volume fractions of the studied samples was obtained as discussed elsewhere [14]. Adding the two components results in a bimodal particle size distribution which corresponds to an effective polydispersity $\sigma = 0.12$. This is sufficient to effectively suppress crystallization in the mixture, thus allowing access to glass transition dynamics even at the longest decay times. Analysing the phase behaviour an interaction potential $u(r) \propto r^{-35\pm2}$ was derived. Thus, the particle interactions are sufficiently hard to closely approximate hard sphere behaviour. At the same time the swelling leads to a significant solvent uptake of the particles (only about 16% of the sphere volume is occupied by polymer). Since the solvent is almost isorefractive and close in density with respect to the polymer, multiple scattering is absent and the particles are effectively buoyancy-matched as well such that the influence of gravity is negligible. That the binary mixture can indeed be mapped onto a one-component hard sphere system with an effective polydispersity of 12% was confirmed by analysis of the volume fraction dependence of the static structure factor [14]. Similarly the glass transition dynamics could be consistently interpreted within MCT in terms of an effective one-component system [40]. A first analysis within the β-scaling law (equation (2) below) provided an exponent parameter $\lambda = 0.78$, a nonergodicity parameter $f^{c}_{q_{\max}} = 0.80$ and a glass transition volume fraction $\varphi_g = 0.596$ [14]. The slight deviations from the reported hard-sphere values ($\lambda = 0.76$, $f^{c}_{q_{\max}} = 0.85$, $\varphi_g = 0.58$) [11, 41] can be explained by the broadening of the particle size distribution [40].

To prepare a non-crystallizing colloid–polymer mixture with a size ratio $\delta = R_{g,\mathrm{polymer}}/R_{\mathrm{colloid}} = 0.054$ (with respect to the average radius of the particles in the binary colloid mixture) varying amounts of linear polystyrene ($R_g = 8.6$ nm, $M_w = 136\,000\ \mathrm{g\ mol^{-1}}$, $M_w/M_n = 1.04$; from Polymer Standards Service GmbH) were added to the binary colloidal mixture of 1:50 crosslinked microgel particles. To this purpose appropriate amounts of dry linear polymer were added to a stock dispersion of the binary mixture and the colloid–polymer mixture was then homogenized by tumbling over several weeks.

2.2. Light scattering experiments

The particle dynamics close to the colloid glass transition were studied with a self-made light scattering setup that is especially optimized for very slow dynamics. The setup has been described elsewhere [42]. Here we only address modifications that have been newly implemented. As compared to previous work, a beam splitter cube has been introduced in order to simultaneously monitor the fluctuations of the scattered intensity by a photomultiplier and by a CCD (charge coupled device). The latter was earlier used separately as an area detector in the so called multispeckle correlation spectroscopy (MSCS) to monitor ultraslow glass transition dynamics or determining the ensemble-averaged intensity autocorrelation function in nonergodic systems by averaging over a large number of independent Fourier components, i.e. speckles [43]. The advantage of simultaneous detection is twofold: the uncertainty of the comparability of MSCS data with standard DLS data of the same sample measured at different times (e.g. due to ageing) is avoided and the time demand per sample is reduced. Due to hardware refurbishing the number of simultaneously detectable speckles has been increased to 300 and the shortest lag times accessible have been reduced to 100 ms. This allows for a better ensemble-averaging and at the same time provides a larger overlap with the traditional DLS curves which are used for normalizing the MSCS curves [43]. A HeNe-laser (JDS Uniphase) with $\lambda = 633$ nm and a power output of 17 mW was used for the measurements.

The determination of the density autocorrelation function $f(q,\tau)$ followed the same strategy as laid out previously [42]. For ergodic samples where the longest relaxation time, i.e. the α-relaxation time τ_α, was much smaller than the chosen sampling time T, the measured intensity autocorrelation function $g_T^{(2)}(q,\tau) = \langle I(q,t) \cdot I(q,t+\tau)/\langle I(q,t)\rangle_T^2$ ($\langle\,\rangle_T$ denotes a time average) was converted into $f(q,\tau)$ using the Siegert relation [44]. For samples close to and above the ergodic–nonergodic transition where τ_α became comparable or longer than the sampling time T the short time behaviour of $f(q,\tau)$ was obtained by standard DLS measurements using the Pusey–van Megen procedure [45] for conversion of $g_T^{(2)}(q,\tau)$ into $f(q,\tau)$. For obtaining the long-time part of $f(q,\tau)$ we used the MSCS method to directly measure the ensemble average of the intensity correlation function $g_E^{(2)}(q,\tau)$ by averaging over 300 independent speckles. To match the MSCS data to the DLS data, the $f(q,\tau)$ curves of the latter were used to calculate the short-time part of $g_E^{(2)}(q,\tau)$ to which the MSCS data were then matched in the overlap region (typically $0.1\ \mathrm{s} \leqslant \tau \leqslant 10\ \mathrm{s}$) and the resulting curve was then reconverted to $f(q,\tau)$, using the Siegert relation in both transformations. Typically, intensity fluctuations have been sampled for a day and the data of five independent measurements have been averaged for each volume fraction close to and above the glass transition. Due to the polydispersity of the mixture no traces of crystallization were detected even over observation times of more than a month.

In order to determine the glass–fluid phase diagram and to establish the glass transition lines it is necessary to distinguish fluid from glassy samples. This task cannot be solved without some ambiguity. In theory, nonergodicity is defined by the occurrence of a non-zero value of the long-time limit of the density correlator $f(q,\tau)$ with the implication that the decay of density fluctuations levels off at a plateau. In experimental practice this condition is, however, rarely met. What is typically observed on approaching the colloid glass transition is the emergence of a plateau which extends for some range of decay times τ and is then truncated by a long-time decay. This is demonstrated in figure 1, where the slowing down of the dynamics of the pure binary mixture is depicted. That this long-time decay is not simply due to instrumental instability can be concluded from the fact that the timescale of this final decay shifts systematically to longer times with increasing packing density. Some of these curves at higher volume fractions do not decay to zero within the experimental probing time. Such samples are not nonergodic in the strict theoretical sense, but ‘non-ergodic on the timescale of the experiment’ with the meaning that some density fluctuations are so slow that they do not decay within the probing time and appear frozen. Pusey and van Megen [45] have shown that this ‘loss’ of the slowest density fluctuations leads to a deviation of the exponential distribution of intensity values characteristic of an ergodic system. As a consequence, the

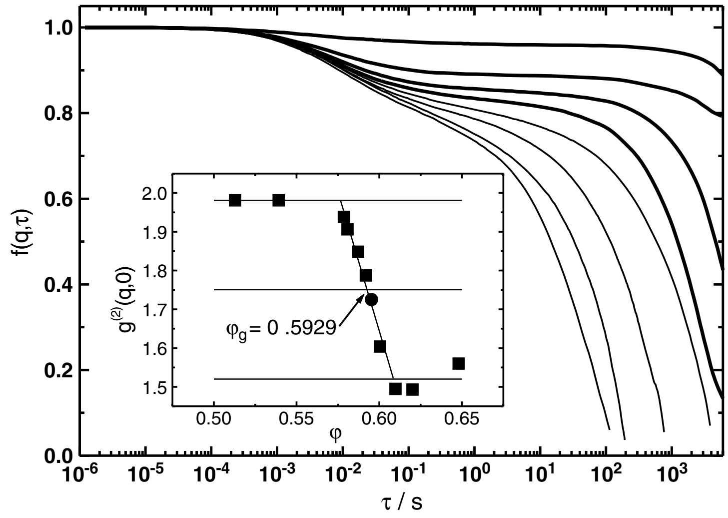

Figure 1. Density correlators $f(q,\tau)$ for a binary mixture of 1:50 crosslinked polystyrene microgel particles with a size ratio of 0.81 and a number ratio small/large of 2.65. The data were taken at $q = q_{\max}$, where $q_{\max}$ corresponds to the peak of $S(q)$. The sample volume fractions are: 0.579, 0.581, 0.587, 0.592, 0.595, 0.6, 0.61 and 0.674 (from left to right). Glass samples are indicated by thick curves. The inset shows the intercepts (■) of the intensity correlation functions of the corresponding samples from which a glass transition at $\varphi = 0.593$ is derived (see text). The solid circle marks the sample at $\varphi = 0.595$ which coincides with φ_g within symbol size.

intercept $g_T^{(2)}(q,0) = \langle I(q,t)^2\rangle_T/\langle I(q,t)\rangle_T^2$, which corresponds to the second moment of the intensity distribution divided by the square of its first moment, is reduced to smaller values than 2, the value characteristic for an ergodic system.

Thus the intercept can be used as a convenient measure to quantify the ‘amount’ of frozen density fluctuations in a system. Its volume fraction dependence for the binary mixture is shown in the inset of figure 1, where averages over repeated measurements have been taken. It starts at a value just below 2 (this difference being due to experimental imperfections), and shows a linear decay in a narrow volume fraction range and levels off at a value around 1.5. This behaviour has been observed for all systems at a colloid glass transition studied so far [42, 46], only the saturation value was found to vary slightly. It corresponds to a narrow transition range within which more and more density fluctuations become frozen. To connect this behaviour to a finite glass transition volume fraction we take the ‘centre of balance’ of the intercept values as indicated by the middle horizontal line and associate the corresponding volume fraction with φ_g. This, at first glance, somewhat arbitrary procedure was found to provide a very good estimate of the location of the glass transition described by MCT [42, 46]. (Note that in earlier work [42] the width of the distribution of intercepts has been used instead of the mean value as in recent work; however, both procedures were found to yield the same result for φ_g.) The φ_g-values found from extrapolation with the various power laws of MCT were always in agreement with those derived from the intercept analysis within experimental accuracy. This is indicated by the solid circle in the inset of figure 1 which indicates the glass transition point as derived from the β-scaling law of MCT (see below). Further support for the correctness of our assignment of samples as glassy is the observation that all samples below the thus determined φ_g show α-scaling, whereas those above violate it [40]. This is already visible in figure 1, where the thin lines show nearly identical line shapes at long times, whereas the first thick line obviously deviates.

While these two procedures to locate the glass transition appear to be very reliable, they are not fully applicable to a colloid–polymer mixture for practical reasons. This would require measuring of the order of ten samples for each of a number of points along the surmized glass transition line in the (Γ, φ) plane, and so the time demand is forbiddingly high. Instead we chose as an operational definition to consider all samples as glassy where the intercepts averaged over a number of measurements was lower than 1.8. This choice was made on the basis of our observation that a moderate reduction of the intercept was found even for samples which were identified as fluid (cf the thin curves in figure 1 and the corresponding squares in the inset).

3. Theory

In the following we will analyse the dynamics of our binary mixture of microgel particles with added linear polymer along the glass transition lines within mode coupling theory. Therefore, we briefly recall the equations necessary for our data analysis. For a detailed description of the theory and its predictions the interested reader is referred to the literature [9, 10, 47].

The structural relaxation of a N particle system is usually described by the autocorrelation function of density fluctuations $f(q, \tau)$,

$$f(q,\tau) = \frac{1}{NS(q)} \sum_{j,k} \left\langle \exp\left\{-\mathrm{i}\vec{q}\vec{r}_j\,(0)\right\} \exp\left\{\mathrm{i}\vec{q}\vec{r}_k\,(\tau)\right\}\right\rangle_E \tag{1}$$

where $\vec{r}_k\,(\tau)$ is the position of particle k at time τ and $\langle\cdots\rangle_E$ indicates an ensemble average. $f(q, \tau)$ is calculated by mode coupling theory via a generalized Langevin equation, the only input necessary being the static structure factor $S(q)$, which in turn can be calculated starting from the interaction potential. At packing densities close to the glass transition the decay of $f(q, \tau)$ to the plateau and the initial decay from the plateau is described by the β scaling law:

$$f(q,\tau) = f_q^c + H(q) g \pm (\tau/\tau_\sigma). \tag{2}$$

This law is the result of an asymptotic solution of the mode coupling equations which describes to first approximation the density correlator in the limits $\varphi \to \varphi_g$ and $|f(q, \tau) - f_q^c| \to 0$. Here, f_q^c is the finite long-time limit to which $f(q, \tau)$ decays at the ideal glass transition. $g_\pm(\tau/\tau_\sigma)$ is a volume fraction and q independent universal master function (the plus sign refers to $\varphi > \varphi_g$ and the minus sign to $\varphi < \varphi_g$), its functional form being fully determined by a single number, the exponent parameter λ, via a combination of two power law expansions, whose exponents a, b and whose expansion coefficients are completely determined by λ [48].

For the long-time decay, $\tau \gg \tau_\sigma$, the so-called α-relaxation, another asymptotic scaling law holds:

$$f(q,\tau) = f_q^c\, G_q\,(\tau/\tau_\alpha)\,. \tag{3}$$

Here $G_q(\tau/\tau_\alpha)$ is a q-dependent master function and the scaling time τ_α obeys another power law:

$$\tau_\alpha = t_0 \left|\frac{\varphi_g - \varphi}{\varphi_g}\right|^{-\gamma}, \qquad \gamma = (1/2a) + (1/2b)\,. \tag{4}$$

The advantage of the above asymptotic solution is that it is easily applicable irrespective of the specific form of the interaction potential as this is contained in the value of the exponent parameter λ, the latter being calculated using the static structure factor of the system of interest. The exponent parameter containing the information about particle interactions is in the following treated as just another fit parameter. In the case of a colloid dispersion where short-ranged attractions are present λ is expected to vary with increasing attraction strength

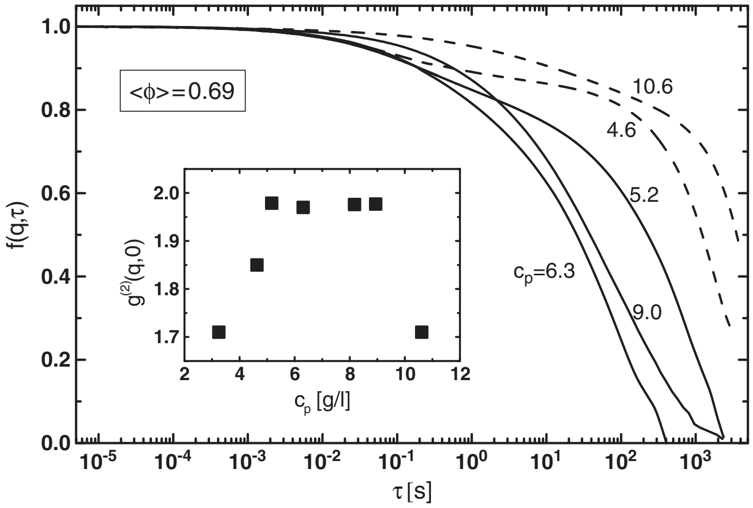

Figure 2. Reentrant glass transition at a colloid volume fraction of 0.69. The polymer (polystyrene) concentration c_p in g l^{-1} is indicated by the numbers at the curves which were measured at q_{max}. The dashed curves represent glassy samples as indicated by the decrease of intercepts shown in the inset. Note the presence of a incipient plateau for the glassy sample at low c_p. This is indicative of the cage effect and is absent in the glassy sample at high c_p, underlining the different nature of the two types of glass states.

(i.e. increasing polymer concentration), increasing from its hard sphere value to a maximum value between 0.9 and 1 (close to an A_3 or A_4 singularity, depending on the attraction range δ) and then decreasing again (cf figure 6 of [21]).

4. Results and discussion

First we want to demonstrate that the reentrant melting region extends to very high volume fractions, much higher than reported for a hard-sphere system [28, 29]. In figure 2 density correlators $f(q, \tau)$ are shown for an average colloid volume fraction of $\langle\varphi\rangle = 0.69$ (the small drift being due to the dilution effect on adding polymer solution to a colloid stock dispersion) and for increasing polymer concentrations c_p ranging from 4.6 to 10.6 g l^{-1}. At a polymer concentration of 4.6 g l^{-1} the sample is glassy, as can be seen from the intercept value which is depicted in the inset. It shows an incipient plateau which is characteristic of a packing-driven glass. The final decay is most likely due to ageing effects. At $c_p = 5.2$ g l^{-1} the sample is in a fluid state, its line shape corresponding to that of a supercooled liquid. The intercept has increased to about 2. Obviously, the small increase of attraction strength corresponding to this slight increase in the polymer concentration is sufficient to melt the glass. At a polymer concentration of 6.3 g l^{-1} the dynamics has sped up by two orders of magnitude and the sample shows an $f(q, \tau)$ which is typical for a normal liquid. On further increasing the polymer concentration the dynamics slows down again and the system undergoes another glass transition between $c_p = 9$ and 10.6 g l^{-1} as is indicated by the intercepts. The density correlator at 10.6 g l^{-1} polymer shows no trace of a plateau and only the value of the intercept indicates that the corresponding sample is nonergodic. The lack of the cage effect indicates that the system has frozen into a bonding-driven glass.

As compared to $\varphi \approx$ constant cuts at lower volume fractions [14, 23] the reentry region is much narrower, corresponding to Δc_p of about 5–6 g l^{-1} as compared to 7–8 g l^{-7} at $\varphi = 0.67$

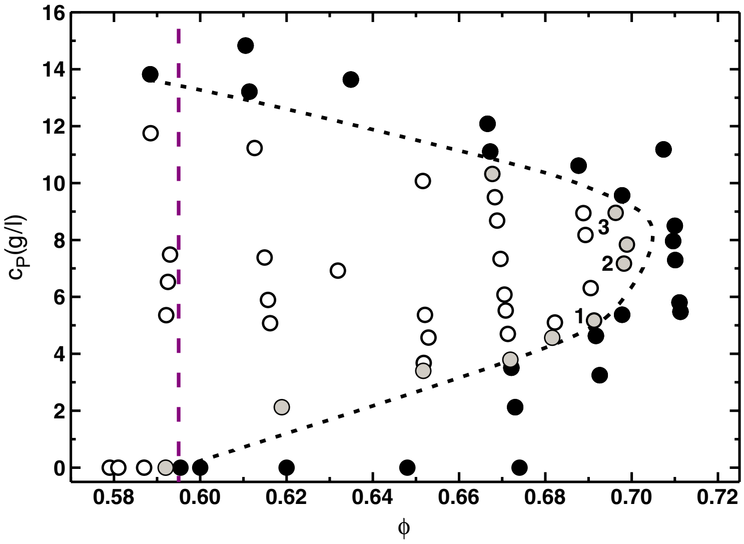

Figure 3. Phase diagram of the binary polystyrene microgel colloid mixture with added linear polystyrene. φ and c_p indicate the colloid volume fraction and the polymer concentration in g l^{-1}, respectively. Open circles represent fluid samples. Solid circles have been identified as glassy samples via the intercept criterion (see text). Shaded circles indicate those samples which were analysed by fitting the density correlators $f(q, \tau)$ with the β-scaling law of MCT, equation (2). The $f(q, \tau)$ of the numbered samples and corresponding fits are shown in figure 4. The extrapolated location of the glass transition line (see text) is shown as a dashed curve. The vertical line gives the glass transition of the pure binary microgel mixture.

and 13–15 g l^{-1} at $\varphi = 0.62$. In order to explore the full reentry region various other cuts at constant volume fraction were made. Figure 3 gives an overview over the measured samples. Samples which showed nonergodic behaviour according to the intercept criterion as explained in section 2.2 are indicated by solid circles, whereas fluid samples are given by the open circles. The dashed vertical line indicates the location of the glass transition of the pure binary mixture. The dotted curve indicates the glass transition line. It has been determined by using the power law for the α-relaxation times τ_α, equation (4), in its linearized form, i.e. $\tau_\alpha^{-1/\gamma} \propto |\varphi - \varphi_g|$. The two samples closest to the transition (as indicated by the nearest glassy sample) in a given region of the phase diagram, figure 3, were taken for extrapolation and the hard sphere value of $\gamma = 2.55$ was employed (a more detailed description of the procedure will be given elsewhere) [40]. As can be seen from figure 3, the extrapolation procedure is consistent with the light scattering data in the sense that all solid circles indicating glassy samples are situated outside the reentry region or on the transition line.

The reentry region in our system is very large, amounting to $\Delta_r = (\varphi_{g,\max} - \varphi_{g,HS})/\varphi_{g,HS} = 0.17$–$0.19$. This is significantly larger than the maximum reentry predicted by MCT [21, 33] which was $\Delta_r = 0.04$–0.05 at much smaller values for the attraction range ($\delta = 0.03$ and 0.01, respectively). It is also much larger than the value for a hard sphere system of PMMA colloids with polystyrene as the non-adsorbing polymer, where it can be estimated to be around $\Delta_r = 0.07$ for $\delta \approx 0.09$ (from figure 1 of [29]). There are different possible reasons for this large reentry region, especially as compared to the PMMA hard sphere system. One obvious possibility is that the particles deform at high volume fraction due to their inherent softness. Another reason could be the occurrence of osmotic deswelling of the particles, an effect that has been reported for microgel particles [49]. A third alternative is polydispersity, i.e. that the broad bimodal size distribution allows for a more efficient packing of the particles.

We think that osmotic deswelling or a permanent deformation can be ruled out as possible causes for the occurrence of an extended reentry region with very high volume fractions in our case. When determining the static structure factors $S(q)$ of our systems we divide the measured static light scattering intensities at high concentrations, which are given by $I_{\mathrm{conc}} \propto P(q)S(q)$ by those measured in dilute dispersion, i.e. $I_{\mathrm{dil}} \propto P(q)$ [24]. Shrinkage of the microgel particles at high concentrations would lead to a shift of the minimum of the form factor $P(q)$ of the spheres as compared to the dilute case. Thus we would divide by a wrong $P(q)$ which would lead to deformations of $S(q)$ which should be easy to detect. This has never been observed even at the highest volume fractions. The same argument applies for a significant sphere deformation. In addition, the repulsive part of the interaction potential is steeper than in the case of a Lennard-Jones potential, making deformations impossible except for short-time collision events. Therefore, a more efficient packing of the microgel spheres due to the broad bimodal particle size distribution is the most likely explanation. From computer simulation studies [50] it is known that polydispersity shifts the volume fraction of random close packing φ_{rcp} to higher packing densities. For polydispersities between $\sigma = 0.1$ and 0.15 one finds $\varphi_{\mathrm{rcp}} = 0.68$, which is, however, considerably smaller than the largest volume fractions achieved in this work. For $\varphi_{\mathrm{rcp}} = 0.71$ the cited simulation study requires $\sigma = 0.3$ which is clearly beyond the polydispersity of our system. However, it has to be considered that in the simulation a Gaussian distribution of particle size was employed. It is reasonable to assume that a bimodal distribution allows for an even more efficient packing of the spheres. In addition, there are indications that in binary mixtures or polydisperse dispersions nanocrystalline order can take place. In a video microscopy study of fluoropolymer/polystyrene microgel core/shell particles we have observed a coexistence of amorphous and nanocrystalline regions [51] and in another microscopy study of binary mixtures of magnetic beads in a thin layer ordering in the form of nanoclusters has been found [52]. Such nanocrystalline order would, indeed, allow for a more efficient packing of spheres.

In the following we will analyse the density correlators of those fluid samples which trace the glass transition line (given as shaded circles in figure 3) with the β-scaling law of MCT, equation (2). For the most interesting samples, indicated as 1–3 in figure 3, the $f(q, \tau)$ curves are depicted in figure 4 together with the corresponding fits. All samples at lower polymer concentrations than sample 1 show line shapes qualitatively similar to this one. The cage effect is present, indicated by the incipient plateau and the density correlators can be well described by a fit with the β-scaling law. This situation changes dramatically when increasing the polymer concentration from 5.2 to 7.2 g l^{-1}. Sample 2 shows a completely different line shape. One finds a monotonous decay without any trace of a plateau. As a consequence only the intermediate region of the $f(q, \tau)$ curve can be fitted by the β-scaling law. In essence this means that only the long-time part of the master function $g_{\pm}(\tau/\tau_{\sigma})$, which is described by a power expansion [48] whose leading term corresponds to the familiar von Schweidler law, $f(q, \tau) = -B(t/\tau_{\alpha})^{b}$, is expressed in the line shape of the correlator. In contrast, the critical decay $(\tau/\tau_{\sigma})^{-a}$ which is the leading term of the short-time expansion of $g_{\pm}(\tau/\tau_{\sigma})$ is absent.

Another feature which distinguishes the line shapes of samples 1 and 2 is the long-time decay. This part of the correlator is typically described by a stretched exponential on approaching the packing driven glass state. In the case of sample 2 one finds, in contrast, indications of a logarithmic decay as indicated by the chained straight line in figure 4(b). This feature is even more pronounced in sample 3, where the $\log(\tau)$ behaviour extends to about two decades in time. At the same time the range of validity of the long-time part of the β-scaling law decreases from four to three orders of magnitude. Even though the observation of

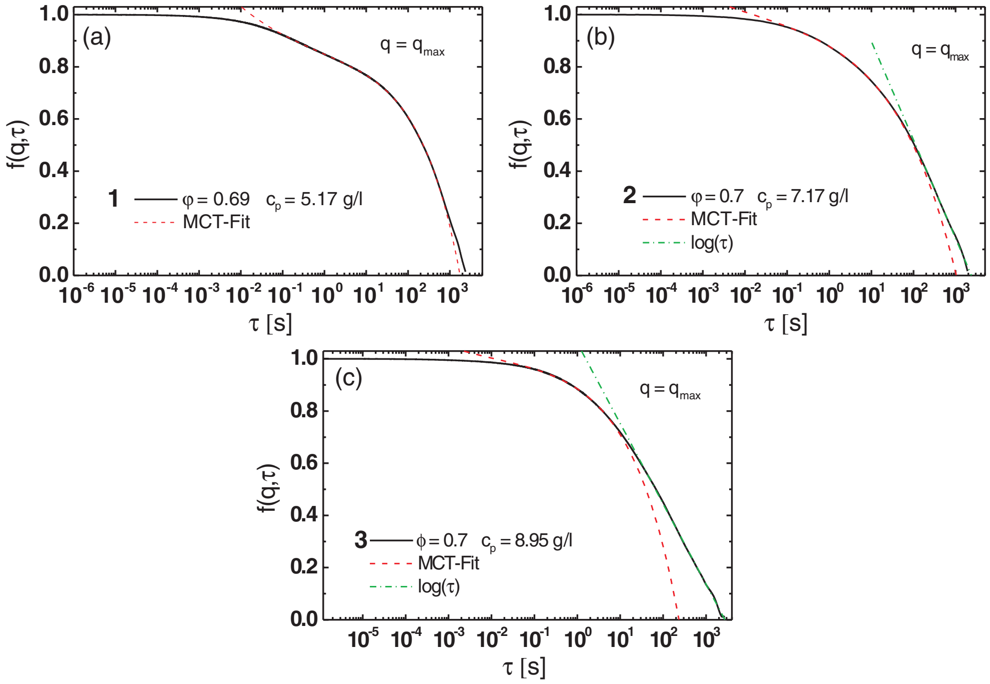

Figure 4. Density correlators $f(q, \tau)$ at $q_{\max}$ of samples marked as 1–3 in the phase diagram figure 4. Dashed curves show fits with the β-scaling law of MCT, equation (2). The chained straight lines indicate that the long-time decays of samples 2 and 3 are exposing logarithmic behaviour.

$\log(\tau)$ behaviour is very intriguing it is by no means clear whether this feature indicates the neighbourhood of a higher-order singularity as apparent log-laws may result as well due to an interplay of different singularities [37–39, 48].

To further elucidate this we reproduce in figure 5 the variation of the exponent parameter λ and the non-ergodicity parameter f_q^c along the transition line as they were obtained by the fits of the density correlators with the β-scaling law, equation (2). Within the considerable scatter of data, which reflects the difficulty to fit with an asymptotically valid scaling law line shapes where the range of validity is unknown and shrinks in an uncontrollable manner along the transition line, the results for λ show qualitatively the trend predicted by theory (cf figure 6 of [21]). One finds that λ increases from the hard sphere value of 0.76, reaches a maximum of 0.91 and then decreases to 0.84 again. Comparing our data with those predicted by theory for $\delta = 0.06$ it is tempting to state a close similarity which would fit nicely in with the value of $\delta = 0.054$ considered to apply for our system. However, this similarity might just be fortuitous, given the scatter in the λ values, the lack of knowledge of how experimental δ-values are mapping onto theoretical δ values and the considerable uncertainty of the correct value of δ for our system (note that there are different numerical relationships between the molecular weight and the radius of gyration for polystyrene chains reported in the literature in addition to the experimental error in the appropriate colloid radius for our binary colloid mixture).

The non-ergodicity parameter f_q^c resulting from the fits shows a sharp increase in a very narrow range of polymer concentrations. This clearly underlines the change in the nearby glass phase from a packing-driven to a bonding-driven glass. Again the qualitative agreement with theoretical predictions (cf figure 7 of [21]) is encouraging. There a sharp jump of f_q^c when crossing the glass–glass transition line was predicted. Here we do not cross this line, but

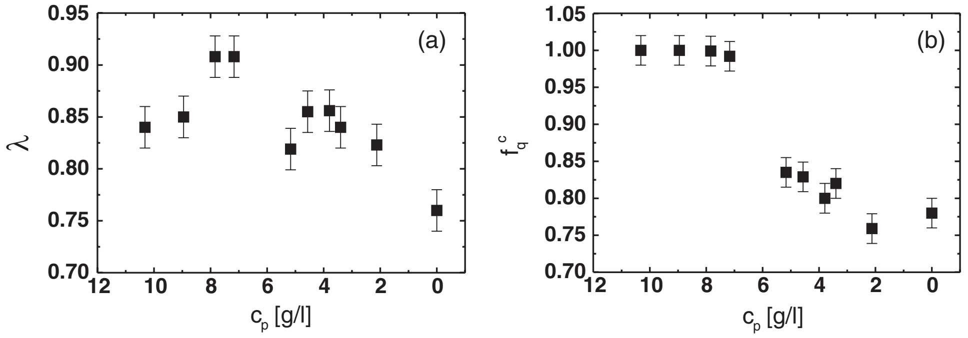

Figure 5. Variation of the exponent parameter λ and the nonergodicity parameter f_q^c along the glass transition lines in dependence of the polymer concentration c_p. The results were obtained by fitting the $f(q,\tau)$ for the samples indicated by the shaded circles in figure 3 with the β-scaling law of MCT, equation (2). Exemplary fits are shown in figure 4.

trace the fluid–glass transition line on the fluid side. Nevertheless, a signature of this jump—possibly smeared out—can be expected to be seen on this path as well [53]. The 'jump' from 0.8–0.85 to 1 in our data, which were taken at the peak of the static structure factor, was much more pronounced than reported by theory (from 0.95 to 1). The non-ergodicity parameter is known to follow the oscillations of $S(q)$ [6, 54]. As the theory data follow a path within the glass state where the peak of $S(q)$ is higher than in the fluid state, this difference is to be expected. In addition, due to the polydispersity the structure factor peak in our system is reduced as compared to a monodisperse system as treated by theory, which may contribute to the difference as well. A similar difference between the nonergodicity parameters of both types of glass was also reported for PMMA hard sphere colloids [29]. There, however, the 'jump' could not be located due to crystallization in the fluid samples close to the transition lines.

In our case the 'jump' in f_q^c and the maximum of the exponent parameter λ allow at least a rough estimate in which range of polymer concentrations a higher-order singularity—if present—should be looked for. It should be close to samples 1 and 2. From the position of these samples in the reentry region and the λ versus c_p data, one can speculate—keeping the problems of mapping and experimental inaccuracies in mind—that an A_4 singularity is close to these samples, however, at a shorter attraction range (i.e. lower value of δ). This is consistent with a recent computer simulation [35] where the A_4 singularity has been located and the dynamics close to it were studied. The density correlators found at q_max for a state point located in a similar region of the phase diagram as our samples 2 and 3 show a close resemblance to our data. In this simulation it is shown that the 'true' $\log(\tau)$-behaviour characteristic of a neighbourhood of a higher-order singularity is visible only at wavevectors much higher than q_max, whereas it is completely masked by corrections to the asymptotic log-law at q_max. Thus, it is very likely that the logarithmic decays seen in our data are only apparent ones, but that nevertheless the corresponding samples are close to an A_4 in (φ, c_p, δ) space. To clarify this point, further experiments are necessary where the wavevector is varied and the attraction range is decreased. Such experiments are currently in progress.

5. Conclusion

The addition of linear polymer to a binary mixture of microgel particles leads to the phenomenon of a reentrant glass transition. The reentry region, determined by applying the power law of mode coupling theory for the α-relaxation times to localize the glass transition lines by extrapolation, was found to be much larger than both predicted by theory and found for PMMA hard sphere colloids. This can most likely be explained to a large extent by the broad bimodal distribution of particle sizes which allows for more efficient packing. Analysing the density correlators by tracing the glass transition lines in the fluid side by the β-scaling law of mode coupling theory we find characteristic changes of the exponent parameter λ and the non-ergodicity parameter f_q^c which are in qualitative agreement with predictions of the theory. The observed 'jump' of f_q^c on increasing the polymer concentration, and thus increasing the attraction strength, is indicative of a change from a packing-driven to a bonding-driven glass. The increase of λ to a maximum value of 0.91 and the subsequent decrease can be interpreted by the neighbourhood of a higher-order singularity. This singularity, if really present, is most likely an A_4 singularity situated at a smaller attraction range (smaller value of δ). To substantiate this speculation further experiments and a careful mapping of experimental control parameters onto those of theory are required.

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