Structure and dynamics of glassy charged colloids studied with coherent small angle X-ray scattering

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Coherent small angle X-ray scattering methods have been used to investigate the structure and dynamics of charged colloidal systems with different volume concentration. The static structure factor indicates that the degree of ordering depends on both the electrostatic interactions and the volume fraction. All systems showed a compressed exponential form of the dynamic structure factor. The $Q$-dependence of the relaxation time $\tau$ hints towards ballistic motion of the colloidal particles in the glassy state. For the sample with the highest volume fraction we observe an influence of the static structure factor on the relaxation rate of the particles indicating a caging effect also for the ballistic type of motion.

1. Introduction

The understanding of the dramatic slowing down and non-exponential relaxations in glasses and dense colloidal suspensions is one of the most challenging problems in condensed matter physics. Recently, the concept of “heterogeneous dynamics” has attracted much attention as it is considered a key ingredient for understanding the drastic slowing down at the glass transition without significant changes in the structure.

A fingerprint of glass-like or jammed systems is that these systems are out-of-equilibrium, so that their properties change continuously with time, while the system slowly evolves towards the equilibrium. Typically, the dynamics become progressively slower as the sample ages and it spends more and more time in the metastable states it visits. The spatial extent of the motions within these systems is extremely reduced and often the dynamic structure factor shows a two-step decay. The commonly accepted physical picture is that the motion of a particle in a disordered, glass-like material is constrained by the “cage” constituted by its neighbors [1]. The dynamics of these systems can be observed with the dynamic structure factor $f(Q, \tau)$. On short times, attributed to the initial fast decay of $f(Q, \tau)$ also referred to as $\beta$-decay, the particles diffuse nearly freely within the cage. On longer time scales, attributed to the final decay of $f(Q, \tau)$ or $\alpha$-decay, the dynamics are frozen, until the particles escape from the cage. This long time motion is subdiffusive and the decay of the correlation function $f(Q, \tau)$ shows a variety of forms.
Indeed both theoretical work and experiments have shown stretched exponential [2], power-law [3] or logarithmic decays [4] as the final relaxation of the dynamic structure factor. Very recently for glassy systems dynamics faster than exponential have been observed [1, 6]. The dynamic structure factor \( f(Q, \tau) \sim \exp[-(\Gamma \tau)^\gamma] \) decays as a "compressed" exponential with an exponent larger than one [1, 5, 7]. In addition for a wide variety of soft materials the characteristic time \( \tau \) for slow relaxation quite often displays an intriguing linear \( \Gamma \sim Q \) scaling. This scaling suggests that the final decay of \( f(Q, \tau) \) is due to a "ballistic" motion of the particles. Therefore, all models based on cage-escape processes have been ruled out and Cipelletti and co-workers proposed instead that the dynamics may be due to randomly distributed internal stress sources acting on the sample [5]. However, most of the systems investigated up to now have been colloidal suspensions of low or medium concentration. In contrast to hard-sphere colloidal suspensions the phase diagram of charged colloidal systems depends not only on the volume fraction but also on the strength of the direct particle interactions. This allows us to distinguish if the caging-effect depends upon the structure or the volume concentration. Here we investigated the structure and dynamics of three charged colloidal systems of different volume concentration with coherent small angle X-ray scattering methods.

2. Experimental part

2.1. Synthesis

2.1.1. Materials
1H,1H,5H- Octafluoropentylmethacrylate (M1), Methacryloxyethyltrimethylsilan (M2) and 2,2,3,3,4,4,5,5-Octafluorohexanediol-1,6-dimethacrylate (M3) were purchased from ACR. \((\text{NH}_4)_{2}\text{Fe(SO}_4\text{)}_2\) and \(\text{NaSO}_4\) were purchased from Fluka and \(\text{K}_2\text{S}_2\text{O}_8\) was purchased from Merck. Tetraethoxysilane (TEOS), ethanol and ammonia (25% by weight) were purchased from Sigma Aldrich.

2.1.2. Silica particles
The silica particles were prepared according to a Stöber polycondensation [8]. A solution of 8 ml TEOS in 500 ml ethanol was prepared. Under stirring at room temperature, the polycondensation was started by the addition of 15 ml aqueous ammonia. After stirring for 24 h, the resulting suspension was filtered and dialyzed against distilled water for one week. Hereby the suspending medium is exchanged from ethanol to water and impurities of small molecular weight are removed. Afterwards the colloidal suspension was concentrated by vacuum evaporation of the solvent and soft centrifugation of the particles.

2.1.3. Perfluorinated polyacrylate particles [9]
The reaction vessel was a 2.5-L three-neck flask equipped with a reflux condenser, a nitrogen inlet tube, and a magnetic stirrer which was set to a stirring speed of 700 rpm during the whole synthesis process. 1.5 l of water was added to the flask and saturated with nitrogen to remove the oxygen in the water. The reaction vessel was heated to 65 °C and a monomer mixture consisting of 0.04 mol of M1, 0.04 mol of M2 and 100 \(\mu\)l of M3 was added. As a redox system a solution of 400 mg of \(\text{NaSO}_4\) and 5 mg of \((\text{NH}_4)_{2}\text{Fe(SO}_4\text{)}_2\) in 10 ml of deionized water was added. The reaction was initialized by adding a solution of 800 mg \(\text{K}_2\text{S}_2\text{O}_8\) in 25 ml of deionized water. After stirring for 24 h, the resulting suspension was filtered and dialyzed against distilled water for one week.

2.1.4. Core-shell particles [10]
The preparation of the inorganic/organic hybrid core-shell particles is a two step procedure consisting of a Stöber polycondensation for the fabrication of the silica cores as described in 2.1.2 and covering them by a perfluorinated polymer shell in a subsequent step in a similar manner as described in the section 2.1.3. In this step, the preparation of the shell starts from a dilute suspension of dialyzed silica.
spheres in distilled water. Therefore, approximately one quarter of the silica spheres obtained from the first step are stirred in 1500 ml of distilled water and heated to 65 °C under nitrogen atmosphere to remove oxygen. To this suspension a Fe$^{2+}$/Fe$^{3+}$/HSO$_3^-$ redox catalyst prepared from 5 mg (NH$_4$)$_2$Fe(SO$_4$)$_2$ and 300 mg NaHSO$_3$ is added. The polymer shell is produced by the radical induced polymerization of M1. By means of a two channel peristaltic pump, during 24 hours 20.0 ml of the monomer M1 and 400 mg of K$_2$S$_2$O$_8$ dissolved in 20 ml distilled water are added via Teflon capillaries immersed in the strongly stirred suspension. Hereby the concentration of radicals and monomer is kept low to suppress the formation of new nuclei forming pure polymer colloids and to promote the growth of long polymer chains entangling the silica spheres. At the end of the reaction, the suspension is filtrated and again dialyzed for one week against distilled water. For all three systems, stray ions are removed by means of a mixed bed ion exchanger leading to opalescent colloidal liquids indicating short range order of the colloidal particles at interdistances comparable to visible light.

Charged colloids can self-organize into liquid-like, crystalline or glassy structures depending upon the concentration of the colloidal suspensions. The colloidal samples are concentrated by gentle centrifugation within the quartz capillaries. For the further investigation of the dynamics we have chosen three different charged colloidal systems. Sample A is a silica colloid (an inorganic charged colloid), sample B is a perfluorinated polyacrylate (an organic charged colloid) and sample C is an inorganic/organic core-shell system consisting of a silica core and a perfluorinated polyacrylate shell. They not only differ in their composition, but also in their volume fraction and size (table 1). In addition, we added to sample A 10 μM KCl and to sample B 50 μM KCl. Sample C is without any added salt.

| Sample | Material | $R$ [nm] | $\Delta R/R$ | $Q_{max}$ [nm$^{-1}$] | $S(Q_{max})$ | $\phi$ | $C_{KCl}$ [μM] |
|--------|----------|---------|-------------|----------------|-------------|-------|-------------|
| A      | Silica   | 101.8   | 0.063       | 0.038          | 2.2         | 0.51  | 10          |
| B      | Perfluorinated polyacrylate | 107.0   | 0.054       | 0.032          | 4.2         | 0.47  | 50          |
| C      | Silica (core) perfluorinated polyacrylate (shell) | 48.6    | 0.032       | 0.049          | 2.8         | 0.17  | 0           |

2.2. X-ray scattering experiments

X-ray photon correlation spectroscopy (XPCS) experiments were performed using partially coherent X-rays at the Troika beamline (ID10A and ID10C) of the European Synchrotron Radiation Facility (ESRF) in Grenoble, France. A Si (111) monochromator was used to select 8 keV X-rays, with a relative bandwidth of $10^{-4}$. A Si mirror downstream of the monochromator suppressed higher-order harmonics of the undulator spectrum. A transversely coherent beam was defined by slit blades with highly polished cylindrical edges. The slit size was 20 microns in both dimensions. Under these conditions, the partially coherent X-ray flux was $10^9$ photons/s. The scattered photons were detected by a direct illumination charged coupled device (CCD) camera from Princeton (20×20 μm$^2$ pixel size used at ID10C) and from Andor (13×13 μm$^2$ pixel size used at ID10A) which were placed 3.30 and 2.14 m behind the sample, respectively. For each sample a series of 1000 CCD images with typical exposure times of 1 s were measured. The electronic background was determined by dark exposures of the CCD camera and subtracted from the data.
3. Scattering theory

3.1. Static behaviour measured with small angle X-ray scattering (SAXS)

Scattering experiments give access to the form factor and static structure factor of colloidal suspensions by measuring the scattered intensity \( I(Q) \):

\[
I(Q) \propto P(Q) S(Q) .
\]  

The form factor \( P(Q) \) is due to the shape of the particles and can be determined from a dilute sample if the interactions of the particles are screened and – as a consequence of the random order under this condition - the static structure factor \( S(Q) \) equals unity.

For spherical particles the form factor is given by:

\[
P(Q) = 9 \left( \frac{\sin(QR) - \cos(QR)}{(QR)^3} \right)^2 .
\]  

The static structure factor \( S(Q) \) describes the interparticle structure of the colloidal dispersion and can be obtained by dividing the scattered intensity \( I(Q) \) by \( P(Q) \).

Since colloidal systems have a certain polydispersity \( \frac{\Delta R}{R} \), for the form factor the Schulz-Flory distribution

\[
f(R, R_0, Z) = \frac{1}{\Gamma(Z+1)} \left( \frac{Z+1}{R_0} \right)^{Z+1} R^Z \exp\left( -\frac{Z+1}{R_0} R \right)
\]  

was taken into account, where \( R_0 \) denotes the number averaged size of the particles. The polydispersity

\[
\frac{\Delta R}{R} = \left( \frac{\langle R^2 \rangle}{\langle R \rangle^2} - 1 \right)^{1/2}
\]

is related to the parameter \( Z \) of the Schulz-Flory distribution by

\[
\frac{\Delta R}{R} = (Z + 1)^{-1/2} .
\]

For core-shell particles with an outer shell radius \( R \) and a ratio of the radii \( \beta = R_c/R \) the form factor is more complex than the standard expression for spheres and it can be calculated via:

\[
P(Q, R_0, \beta_0, Z_R, Z_\beta, \rho_1, \rho_2) = \int_0^\infty f_1(R, R_0, Z_R) \int_0^\infty f_2(\beta, \beta_0, Z_\beta) \alpha(R, \beta, \rho_1, \rho_2)
\]

\[
\left( \frac{3}{(QR)^3} \beta^3 \rho_1 + (1-\beta^3) \rho_2 \right)^2 \times \rho_1 \left[ \sin(\beta QR) - \beta QR \cos(\beta QR) \right]
\]

\[
- \rho_2 \left[ \sin(QR) - QR \cos(QR) - \sin(\beta QR) + \beta QR \cos(\beta QR) \right]^2 d\beta dR ,
\]  

(4)
where \( \rho_1 = \rho_C - \rho_0 \) and \( \rho_2 = \rho_S - \rho_0 \) are the differences in the electron densities between the core \( \rho_C \) and the medium \( \rho_0 \) and between the shell \( \rho_S \) and the medium, respectively. The form factor is weighted by the product of a Schulz-Flory-distribution \( f_1 \), which describes the possibility to find a particle with the outer shell radius \( R \) and arbitrary core-to-shell ratio and a second, mapped Schulz-Flory-distribution \( f_2 \), which describes the probability to find a given core-to-shell ratio \( \beta \). Finally, \( \alpha(P, \beta, \rho_1, \rho_2) \) is the volume weighted contrast of the core-shell particles [11].

3.2. Dynamics via XPCS

A coherent X-ray beam scattered from a disordered system produces a random diffraction or ‘speckle’ pattern which is related to the exact spatial arrangement of the particles in the sample. If the spatial arrangement of the disorder changes with time the corresponding speckle pattern will also change and the intensity fluctuations of the speckles provide a measure of the underlying dynamics [12]. From the intensity fluctuations the normalized intensity autocorrelation function can be calculated:

\[
g_2(Q, \tau) = \frac{\langle I(Q,t)I(Q,t+\tau) \rangle}{\langle I(Q,t) \rangle^2} = 1 + A |f(Q, \tau)|^2, \tag{5}
\]

where the angular brackets denote the time average and \( A \) is the speckle contrast. The intermediate scattering function \( f(Q, \tau) \) is related to the structure factor via

\[
f(Q, \tau) = \frac{S(Q, \tau)}{S(Q, 0)}.
\tag{6}
\]

In the case of heterogeneous dynamics the decay of the intermediate scattering function \( f(Q, \tau) \)

\[
f(Q, \tau) = \exp\left(-(\gamma \tau)^\gamma\right)
\tag{7}
\]

can phenomenologically be described by a compressed exponential form with an exponent \( \gamma \) larger than 1. Usually \( \gamma \) is in the range between 1.5 and 2 [1]. Typically for heterogeneous dynamics this phenomenon is accompanied by a linear dependence of the relaxation rate \( \Gamma \) on \( Q \). Thus the diffusion process is a ballistic type of motion which is a common feature for jammed and hyper-diffusive systems [1].

Equation (5) represents a time average and is therefore not sensitive to temporal heterogeneities. In the case of temporal heterogeneities the dynamics depend on the time interval investigated. In this case the two-time intensity correlation function allows studying non homogenous dynamics and also aging phenomena. It is calculated according to [13]

\[
c_2(\tau_1, \tau_2) = \frac{\langle I_p(\tau_1)I_p(\tau_2) \rangle_{pix}}{\langle I_p(\tau_1) \rangle \langle I_p(\tau_2) \rangle_{pix}} - 1
\tag{8}
\]

Here, the averages are performed over a region of interest of the CCD detector, all having the same \( |Q| \)-value. Important variables for the two-time correlation function are the average time or age of the sample given by \( (\tau_1 + \tau_2)/2 \) measured along the diagonal of \( c_2 \) with \( \tau_1 = \tau_2 \) and the time difference \( \Delta \tau = \tau_1 - \tau_2 \) which is measured perpendicular to the diagonal direction. In an equilibrium system, the two-time correlation functions depend only on the time difference \( \Delta \tau \), and hence the two-time correlation contour lines are parallel. In such a situation the usual one-time correlation function is retrieved by averaging the two-time correlation function over different ages.
4. Results and Discussion

4.1. Structure of the colloidal systems

The size and polydispersity of the colloidal particles were obtained from the form factor of the particles. The form factor was determined from a dilute suspension whose electrostatic interactions were screened by 10^3 mol·l⁻¹ potassium chloride so that the static structure factors equal unity. The overall radius for sample A and B were determined to 101.8 nm (ΔR/R = 0.063) and 107.0 nm (ΔR/R = 0.054) with a form factor for spherical particles (equation (2)) under assumption of a Schulz-Flory size distribution (equation (3)), respectively. In the case of the inorganic/organic core-shell particles (sample C) the form factor for core-shell systems (equation (4)) was used and the overall radius of the particles was determined as 48.6 nm (ΔR/R = 0.032). For sample C smaller particles can be used compared to sample B since the high electron density provided by the silica core yield similar scattering intensities. With the smaller particles lower volume concentrations with strong ordering tendencies were achieved.

The static structure factors were obtained by dividing the scattered intensity of the concentrated suspensions by the diluted suspensions whose electrostatic interactions were screened by 10^3 mol·l⁻¹ potassium chloride. Finally, the data were rescaled by the ratio of number densities of the diluted to the concentrated sample.

The position of the first peak in S(Q) (figure 1) indicates the different volume fractions of the samples. A least squares fit to the static structure factors applying the rescaled mean sphere approximation (RMSA) yields a good approximation of the volume fraction of the colloidal systems [14]. S(Q) for Sample A peaks at the largest value of QR and we estimate via RMSA a volume fraction of ϕ = 0.51. Despite the high volume fraction the peak height of S(Q) is only 2.2, indicating a rather low degree of interparticle correlation. In contrast, Sample B is more structured showing a high S(Q) peak value of 4.2. The sample is still in a disordered state as no Bragg peaks are visible in the 2D-diffraction pattern. From the first peak of the structure factor we estimate via the RMSA a volume fraction of ϕ = 0.47. Sample C exhibits the lowest QR value and accordingly the lowest volume fraction of ϕ = 0.17. Despite the low volume fraction the structure peak is clearly visible with a peak value of 2.85. Thus according to the Hansen-Verlet criteria (S(Q)>2.85) [15], sample B and C can be assumed to be in the glassy phase. Similar concentrations for glassy materials were also found for charged colloidal system from other groups [16-18]. Despite the low peak value of sample A its dynamics also show glass like features.

The interparticle correlation depends not only on the volume fraction, as in the case for hard spheres, where above ϕ = 0.56 the glass transition is reached [19-21], but additionally depends on the long-range electrostatic interactions in the sample. The higher the electrostatic interactions are, the more ordered are these systems. Moreover, the electrostatic interactions depend on the surface charges of the particles. In case of silica particles the charges on the surface stem from hydroxy-groups and for the perfluorinated polyacrylate systems from HSO₃⁻-groups resulting from the initiator during the synthesis process. The latter one provides a significantly higher surface charge than the first one. In both cases the interactions can be screened by adding electrolyte like potassium chloride. If the surface charges are not screened, these high surface charges from HSO₃⁻-groups can result in a highly ordered structure even at comparatively low volume fractions as shown in case of sample C. With increasing ionic strength of the medium the electrostatic interactions are screened, resulting in a more and more hard-sphere like potential. For such systems the critical volume fraction for the glass transition is much higher than for a system with long range interactions. The system of weakly charged silica spheres shows even at volume fractions close to a dense packing only a maximum of the static structure peak S(Q)=2.2. A summary of the sample properties are given in table 1.
Figure 1. Static structure factors $S(QR)$ of the samples A, B and C which differ in composition, size, volume fraction and added electrolyte. The shift to lower $QR$ values from top to bottom is due to increasing interparticle distances resulting from decreasing volume fractions of the samples.
4.2. Dynamics

Figure 2 displays the two-time correlation functions of the different samples obtained by applying equation (8) to the series of CCD images at a fixed \( Q \)-position. All correlation functions display features typical for out-of-equilibrium systems. In the first case for sample \( A \), the dynamics progressively slow down with time (figure 2(a)), but at some points in time the motion accelerates again which indicates the heterogeneity of this sample. Contrary to sample \( A \), sample \( B \) does not display heterogeneity (figure 2(b)), however an aging is visible by a slowing down of the dynamics over the whole time period. This phenomenon of aging of the sample or slowing down of the motion has also been seen by Cipelletti [5]. Sample \( C \) shows very heterogeneous dynamics with strong fluctuations (figure 2(c)). In the two-time correlation function of sample \( C \) obviously a two-step process is present and no aging is visible in the spectra.

![Figure 2](image-url)

**Figure 2.** Two-time correlation functions for the three different samples \( A, B \) and \( C \) show the time evolution of the dynamics in these systems. The two-time correlation functions were calculated for the \( Q \)-value at the peak position of the static structure factors.

From the \( g^2 \)-function and the speckle contrast the dynamic structure factor \( f(Q, \tau) \) is calculated. For all three samples the correlation functions \( f(Q, \tau) \) are fitted best with a compressed exponential, equation (7), with an exponent \( \gamma \) larger than 1.75. In addition, the compression exponent \( \gamma \) increases with the degree of heterogeneity of the sample as indicated by the fluctuations of the two-time correlation function (figure 2). Sample \( B \) exhibits the lowest compression exponent with \( 1.75 \pm 0.17 \) (figure 3(b)). Sample \( A \) can be described with a slightly higher compression exponent of about \( 1.85 \pm 0.13 \) (figure 3(a)). For sample \( C \), the two-time correlations show very heterogeneous dynamics and the compression exponent \( \gamma \) reaches values up to \( 2.19 \pm 0.12 \) (figure 3(c)). For sample \( C \) a second exponential decay is clearly visible. For the other two samples at least an indication of a second decay appears, but not as pronounced as for sample \( C \). The relaxation rate \( \Gamma \) shows a linear dependence on \( Q \) which is a typical indication for ballistic nature. Only for sample \( A \) the relaxation rate \( \Gamma \) shows a minimum at the peak position of the static structure factor (figure 4(a)), indicating that the dynamics here are still influenced by caging effects. This implies that above a certain volume fraction the nearest-neighbors interactions are locally dominating the dynamics, even if the system shows ballistic dynamics.
Figure 3. The dynamic structure factor of sample A, B and C for different $Q$-values. They all show a compressed exponential behaviour for the first decay which can be described by a $\gamma$-value of about $1.85 \pm 0.13$ for sample A, $1.75 \pm 0.17$ for sample B and $2.19 \pm 0.12$ for sample C. The $\gamma$-value increases when the sample shows a more pronounced heterogeneous behaviour. For sample C a second decay is clearly visible in the dynamic structure factor.
Figure 4. The static structure factor $S(Q)$ and the relaxation rate $\Gamma$ of Sample A, B and C vs Q.
5. Conclusion
In this study we compare the dynamics of three charged colloidal systems. All samples showed a high ordering tendency as evidenced from their static structure factor. The two-time correlation functions revealed both heterogeneity of the dynamics and aging of the samples. For all samples we observe a peculiar compressed exponential shape of the dynamic structure factor with a compression factor $\gamma$ larger than 1.75. The inverse relaxation time $\Gamma$ shows a linear dependence on $Q$ which can be attributed to a ballistic motion of the colloidal particles. For the highest volume fraction we also observed the caging effect in the ballistic motion, i.e. $\Gamma$ shows a minimum at the peak position of the static structure factor.

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7. References
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