Anomalous Dynamics of Concentrated Silica-PNIPAm Nanogels

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Abstract

We present the structure and dynamics of highly concentrated core-shell nanoparticles composed of a silica core and a poly(N-isopropylacrylamide) (PNIPAm) shell suspended in water. With X-ray photon correlation spectroscopy we are able to follow dynamical changes over the volume phase transition of PNIPAm at $LCST = 32^\circ$. On raising the temperature beyond $LCST$, the structural relaxation times continue to decrease. The effect is accompanied by a transition from stretched to compressed exponential shape of the intensity autocorrelation function. Upon further heating we find a sudden slowing down for the particles in their collapsed state. The q -dependence of the relaxation time shows an anomalous change from $\tau_c \propto q^{-3}$ to $\tau_c \propto q^{-1}$. Small angle x-ray scattering data indicate a temperature-induced transition from repulsive to attractive forces. Our results indicate a temperature-induced phase transition from a colloidal liquid with polymer-driven dynamics towards a colloidal gel.

Graphical TOC Entry

Stimulus-responsive nanogels offer numerous applications in technical as well as medical fields.^{1,2} Moreover, they are a popular model system to probe the specific phase behaviour of cross-linked soft colloids.³ Poly(N-isopropylacrylamide) (PNIPAm) is a frequently studied system which has shown applications in biomedicine as a sensor or for controlled and triggered drug delivery.^{4,5} As a thermosensitive nanogel PNIPAm undergoes a reversible volume phase transition at a lower critical solution temperature (LCST) in water around 32°C since the polymer changes from hydrophilic to hydrophobic.⁶ The consecutive imbalance between attractive and repulsive forces in the particles results in a rapid collapse of the particle volume with increasing temperature.^{1,7-9} Whereas the dynamics of the swelling-deswelling process has been studied frequently on PNIPAm hydrogels,^{10,11} PNIPAm nanogel particles represent an ideal model system to investigate the phase transition, interaction and dynamics of soft colloidal particle suspensions. Several light scattering experiments have been performed to study the influence of concentration on the swelling behaviour of pure PNIPAm nanogels with respect to structural correlations.¹²⁻¹⁴ However, in these experiments PNIPAm nanogels with concentrations of only up to 2 wt% could be characterized. X-ray photon correlation spectroscopy (XPCS) enables the investigation of structure and dynamics of highly concentrated colloidal systems^{15,16} which cannot be accessed by laboratory-based techniques such as dynamic light scattering (DLS). XPCS has become an established technique to study the dynamics of disordered systems on the nanometer length scale. In the present case we investigate the change in structure and dynamics of concentrated PNIPAm nanogels around the LCST via XPCS. Since the polymer itself shows a low electron density difference with the surrounding water^{11,17} we extend the scattering contrast by using a core-shell system^{12,18} with a strongly scattering SiO₂ core coated by a cross-linked PNIPAm shell.¹⁹ Temperature- and scattering vector q dependence of the characteristic relaxation time as well as the slope of the intensity correlation functions give rise to dynamical anomalies present in the phase transition in a highly concentrated soft colloidal system.

In both DLS and XPCS experiments the normalized second order intensity correlation

function g_2 is determined as the function of wavevector transfer q and time τ ²⁰

$$g_2(\mathbf{q}, \tau) = \frac{\langle I(\mathbf{q}, 0) I(\mathbf{q}, \tau) \rangle}{\langle I(\mathbf{q}) \rangle^2} = 1 + \beta(\mathbf{q}) \cdot |f(\mathbf{q}, \tau)|^2, \quad (1)$$

where $\langle \cdot \rangle$ denotes the time average. Hereby $q = n \cdot \frac{4\pi}{\lambda} \sin \frac{2\theta}{2}$, with refractive index n ($n \approx 1$ for X-rays²¹), wavelength λ and scattering angle 2θ). The second part of Eq. (1) is known as Siegert-relation where $\beta(\mathbf{q})$ is the speckle contrast depending on the coherence of the source.²⁰ For lasers the contrast is typically close to 1, for X-rays β is setup-dependent. For the experiment reported here the contrast was found to be around 0.15. For many soft matter systems the intermediate scattering function $f(\mathbf{q}, \tau)$ can be expressed by the Kohlrausch-Williams-Watts (KWW) function as

$$f(\mathbf{q}, \tau) = \exp(-(\Gamma(\mathbf{q})\tau)^\gamma) \quad , \quad (2)$$

containing information about the dynamics of the system²² with the Kohlrausch exponent γ and the relaxation rate $\Gamma(q)$ which is related to the relaxation time τ_c via $\Gamma = \tau_c^{-1}$. For diffusive systems the relaxation rate is given by

$$\Gamma(q) = D \cdot q^2 \quad (3)$$

where D is the (Stokes-Einstein) diffusion constant.²³ The hydrodynamic radius R_H of the particles can be determined from the DLS intensity-intensity correlation function via the Stokes-Einstein relation

$$R_H = q^2 \cdot \frac{k_B T}{6\pi\eta\Gamma} \quad , \quad (4)$$

with η as viscosity of the solvent, in our case H₂O. For non-diffusive dynamical processes this q -dependence differs from the quadratic form. Hence, τ_c as a function of q contains information about the respective underlying dynamics in the system which can be typically described by a power law $\tau_c \propto q^{-p}$. Additionally, the characteristic dynamics influences the

slope of $g_2(q, \tau)$, quantified by the Kohlrausch exponent γ . For simple diffusion, the decay is exponential with $\gamma = 1$. A stretched ($\gamma < 1$) exponential decay together with $p > 2$ shows sub-diffusive behaviour,^{24–26} while a compressed ($\gamma > 1$) exponential slope with $p \leq 2$ indicates hyper-diffusive, ballistic-like dynamics.^{27,28} A transition between different types of slopes indicates, e.g., the existence of heterogeneities as often seen in glass formers.^{29,30}

DLS measurements were performed on silica-PNIPAm particles in aqueous suspensions between 15°C and 45°C in order to determine the temperature-dependent deswelling behaviour. As shown in Fig. 1a the hydrodynamic radius shrinks linearly upon heating until it decreases dramatically at 32°C. Above 37°C the radius is constant at $R_H \approx 70$ nm. This behaviour with 32°C as critical transition temperature has been seen in several studies on pure PNIPAm.^{31–33} In the hydrophobic state the radius of the core-shell particles is about

Figure 1: (a) Temperature-dependent hydrodynamic radius R_H of Silica- PNIPAm particles characterized by DLS. (b) SAXS results: (◊) $I(q)$ of diluted sample with a spherical core-shell form factor $P(q)$ at 20°C, (◻) $I(q)$ of concentrated sample upon heating from 15°C (blue) to 45°C (red). The data is shifted vertically for clarity.

70 nm, while it was about 130 nm for the lowest temperature where the PNIPAm shell is

completely swollen. The uncoated silica particles were as well characterized by DLS and found to have a hydrodynamic radius around 54 nm. This leads to a shell thickness of about 75 nm in the swollen state and 16 nm in the collapsed state. When passing the LCST the volume of a single particle is thus reduced by 84%. With this an effective volume fraction of $\phi_{\text{eff}} \approx 55 \text{ vol\%}$ can be calculated for the system of swollen particles at 20°C.

Fig. 1b shows the azimuthally averaged intensity profile $I(q)$ obtained from SAXS of a diluted suspension with $w = 3.50 \text{ wt\%}$ at 20°C (black $\diamond$). Since inter-particle interactions are negligible for such low concentrations the data can be described with the form factor $P(q)$ of a spherical core shell system with a Schulz-Zimm size distribution (shown by the red solid line). Due to the high electron density of silica compared to PNIPAm the scattering signal is dominated by the core. The model thus integrates mainly over the core and gives a radius of 51 nm. Fig. 1b further shows all $I(q)$ of the concentrated sample (coloured $\triangleright$) obtained upon heating from 15°C to 45°C. All intensity profiles between $T = 15^\circ\text{C}$ and 36°C resemble each other in the whole covered q range. The scattering signal hence arises mainly from the core with no influence of the PNIPAm shell in this temperature regime. Upon heating from $T = 37^\circ\text{C}$ to 45°C the intensity profiles start to decrease continuously in magnitude for $0.026 \text{ nm}^{-1} < q < 0.055 \text{ nm}^{-1}$. The change in signal can be attributed to the collapsing PNIPAm-shell since the minimum at $q = 0.085 \text{ nm}^{-1}$ remains temperature independent for all $I(q)$, independent of temperature and thus arises from the spherical form factor of the silica particles. However, for $T > 37^\circ\text{C}$, the q regime of the decrease in intensity corresponds to a scale in the range of the particle size including the shell. The downturn in $I(q)$ in that q range suggests the appearance of attractive forces in the system³⁴ once the shells of the particles are fully collapsed at $T = 38^\circ\text{C}$ (compare R_H in Fig. 1a).

For XPCS the scattering intensity and hence the accessible q range was limited due to the short exposure time of $\tau = 0.5 \text{ ms}$. In Fig. 2 the intensity correlation functions are shown for all temperatures at a selected q -value of 0.02 nm^{-1} with the corresponding KWW fit (Eq. 1 and 2). All g_2 functions are normalized to the speckle contrast $\beta \approx 0.15$. Upon

Figure 2: Temporal evolution of the corresponding correlation functions (a) for temperatures between 15°C and 36°C where the system speeds up and (b) between 37°C and 45°C where the system slows down, respectively. The increase of the temperature is indicated by the black arrow in both figures. The g_2 functions were calculated at $q = 0.02 \text{ nm}^{-1}$, the solid lines represent the KWW functions.

heating until 36°C the correlation function shifts towards shorter relaxation times which implies faster dynamics of the particles. Interestingly for temperatures higher than 32°C also the slope changes, indicating a dynamical transition of the system. At 37°C the system rapidly slows down evident by a jump of the correlation function towards larger times and displays two relaxation processes. For this temperature the model had to be extended to a double exponential:

$$g_2(\mathbf{q}, \tau) = 1 + (\beta - \alpha) \cdot \exp[-2(\Gamma_1(\mathbf{q}) \cdot \tau)^{\gamma_1}] + \alpha \cdot \exp[-2(\Gamma_2(\mathbf{q}) \cdot \tau)^{\gamma_2}]. \quad (5)$$

Two relaxation processes are usually observed for many glass formers near or below the glass transition temperature T_g ^{35,36} or in colloidal gels.³⁷ At 38°C another sudden jump to slower dynamics is observed. The decorrelation of the g_2 -function sets in at $\tau \approx 0.2$ s. Upon further heating up to 45°C the system continues to slow down. During the total exposure time of 2 s no second relaxation process is observed for temperatures $T \geq 38^\circ\text{C}$.

The relaxation times and KWW parameters of the g_2 functions are shown in Fig. 3. Here Fig. 3a contains the corresponding relaxation times of the g_2 functions in Fig. 2. Three regions can be defined in the studied temperature range: In region A for $T < 32^\circ\text{C}$ the relaxation time decreases monotonously from about 1 to 0.1 s. Between 32°C and 36°C (region B) τ_c decreases rapidly from 0.1 to 0.01 s implying a speed-up of the particles. This temperature regime corresponds to the regime where the particles start to collapse (compare Fig. 1a). For $T = 37^\circ\text{C}$, which was chosen to be the border between B and C, both τ_{c_1} and τ_{c_2} are plotted. Here τ_{c_2} (●) relates to a dramatic slow down of dynamics, whereas τ_{c_1} (○) describes a dynamical process comparable to the dynamics at $T = 34^\circ\text{C}$. In region C for $T > 36^\circ\text{C}$ all τ_c are increased by several orders of magnitudes compared to region B. In contrast to the plateau of strongly increased relaxation times typically seen for high packing fractions,³⁸ we here observe a tendency towards higher τ_c with increasing T . In this

regime the g_2 functions do not fully decorrelate within the total exposure time of 2 s. As the g_2 function only drops by 2% for $T = 45^\circ\text{C}$, τ_c is not modeled for this temperature and q -value. In temperature regime C the particles in the dilute suspension were found to be fully collapsed, as shown in Fig. 1.

The character of the dynamics is reflected in the q dependence of the characteristic relaxation time and the Kohlrausch exponent (Fig. 3b). Fig. 3c compares the development of τ_c for 20°C (blue, swollen particles) and 42°C (red, collapsed particles) as a function of wave vector transfer. In either case τ_c shows a distinct q dependence. The solid lines represent fits of a power law $\tau_c \propto q^{-p}$. For $T = 20^\circ\text{C}$ a value of $p \approx 3$ (here $p = 2.92 \pm 0.05$) was found pointing towards an anomalous dynamical behaviour of the swollen particles. While simple Brownian motion where $\tau_c = 1/Dq^2$ (Eq. 3) leads to the mean-squared displacement of the particle $\langle \Delta r^2(t) \rangle \sim t^a$ with $a = 1$, the relation $\tau_c \sim q^{-3}$ can be associated with $a = \frac{2}{3}$.³⁹ A mean-squared displacement with $a < 1$ relates to sub-diffusive particle motion.^{24,25} A scaling of $\tau_c \propto q^{-3}$ has been observed for colloids in a polymer matrix²⁵ where the dynamics of the colloid is linked to the motion of the surrounding polymer chains. This q^{-3} dependence is also observed for membrane-like polymers following the Zimm model.^{39–42} Fig. 3b shows that $2.8 < p < 3.4$ is found in the whole temperature regime A. The result suggests polymer-dominated dynamics below the LCST. We attribute this to the swollen PNIPAm shells functioning as a polymer matrix. Here, silica cores can be associated as tracer particles with their motion dominated by the surrounding polymer network.

The corresponding Kohlrausch exponent in temperature region A was found to be $\gamma \approx 0.5$ with no distinct q dependence (Fig. 3c, left y-axis). This stretched and thus slower than exponential decay of the correlation function confirms the anomalous, sub-diffusive motion of the particles.^{24–26} It further may indicate the presence of dynamical heterogeneity with the presence of multiple structural relaxation processes in the system.⁴³

In contrast, for the collapsed particles at $T = 42^\circ\text{C}$ we found $p \approx 1$ (here $p = 0.91 \pm 0.07$), indicating a dynamical transition of the system upon heating. The according Kohlrausch

Figure 3: (a) Temperature dependence of the characteristic relaxation time τ_c at $q = 0.02 \text{ nm}^{-1}$. Between B and C at 37°C where the g_2 function shows two decays both τ_{c1} ($\bullet$) and τ_{c2} ($\circ$) are shown. (b) Temperature dependence of γ and p at $q = 0.02 \text{ nm}^{-1}$ (the dashed line illustrates the development of both γ and p for simple diffusion). For $T = 37^\circ\text{C}$ γ_1 and γ_2 are shown while p pertains to $\tau_{c2} = 1/\Gamma_2$. (c) q dependence of the Kohlrausch exponent γ and the relaxation time τ_c for 20°C (blue) and 42°C (red).

exponent for this temperature and q -value was found to be $\gamma \approx 1.8$. We attribute the appearance of $\gamma > 1$ together with the q^{-1} relation to ballistic, hyper-diffusive motion often reported for jammed non-diffusive soft materials such as colloidal gels, concentrated emulsions and glasses.^{27,28,37,44–49} In contrast to regime A γ shows a decay as a function of q . While we found $\gamma = 1.8$ at the lowest q probed here it approaches $\gamma \approx 1.5$ with increasing q . A similar trend has been described for soft glassy gels where the KWW exponent is predicted to be 1.5 for $q \rightarrow 0$ and $\gamma = 1.25$ for $q \rightarrow \infty$.^{46,48} The proposed microscopical explanation for this type of dynamics are random micro-collapses of the colloidal gel. The particles strive for a dense packing by local reconstruction of the gel which results in a strain field and thus a movement of other surrounding particles. The observed dynamics in regime C agree with the dynamics in PNIPAm hydrogels where $\tau_c \propto q^{-1}$ and $\gamma > 1$ were found for temperatures both below and above the LCST.^{11,50} Together with the $I(q)$ where indications for the appearance of particle agglomerates due to attractive forces are observed at temperatures matching regime C, the results point towards the formation of a colloidal gel once the PNIPAm shell is fully collapsed. These observations are in line with previous studies on similar colloidal systems, reporting the formation of an attractive, fractal gel.¹⁸ Typically, hyperdiffusive dynamics are interpreted as strain-dominated dynamics in gels, which is extended in recent studies to a model of clustering particles.^{51–53}

Overall, the temperature regimes defined for τ_c apply as well to γ and p (Fig. 3b). With both parameters being constant in regime A at $\gamma \approx 0.5$ and $p \approx 3$ the whole temperature regime can be attributed to sub-diffusive dynamics. Upon heating to 36°C (region B) γ increases gradually but stays in the range of $0.5 < \gamma < 1$. In parallel p rapidly decreases towards $p = 2.5$. This supports the observation of the change from sub-diffusive towards diffusive dynamics, whereas, despite passing the regime, simple diffusion ($\gamma = 1$, $p = 2$) is never adopted as indicated by the dashed line in Fig. 3a. The double exponential decay found at $T = 37^\circ\text{C}$ indicates the appearance of dynamical heterogeneities. This can be rationalized by a first slowdown connected to formation of clusters of arrested particles

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3 followed by a second slowdown of the clusters. Such a gel formation process has been
4 predicted for colloidal particles⁵⁴ and found recently in experiments.⁵⁵

7 Also in region C, the compressed exponent $\gamma > 1.5$ is found for the whole temperature
8 regime. At the same time p decreases towards unity. Hence, upon heating and thus de-
9 swelling of the PNIPAm-shell the system undergoes a phase transition from a polymer-
10 dominated liquid with sub-diffusive motion to a jammed colloidal gel with hyper-diffusive
11 behaviour. This is connected to a structural transition from a repulsive system in the fluid
12 regime⁹ to an attractive colloidal gel^{12,18} for the collapsed nanogels.

19 In conclusion, we determined the temperature-dependent structure and dynamics of con-
20 centrated silica-PNIPAm core-shell nano particles in the vicinity of the volume phase tran-
21 sition at the LCST. The XPCS results show a precise classification of the dynamics in three
22 temperature regimes visible in the q - and temperature-dependence of the intensity correla-
23 tion functions. We found regime A as the low temperature regime where the particle motion
24 was found to be sub-diffusive with $\gamma < 1$ and the anomalous relation of $\tau_c \sim q^{-3}$. In this
25 regime the PNIPAm shell is swollen and the particles can interpenetrate and deform^{56,57}
26 which leads to the model of a polymer network with silica as quasi-tracer particles whose
27 dynamics are dominated by the surrounding polymer chains. Passing the LCST an interme-
28 diate region B was defined. The rapid collapse of the particles in this temperature regime
29 B is reflected by an strong increase of the relaxation rate pointing out a sudden slow down
30 of the system at 37°C. The appearance of a double-exponential decay of the g_2 function at
31 $T = 37^\circ\text{C}$ further indicates a two-step gelation mechanism. In the upper temperature region
32 C a compressed relaxation is present with $\gamma > 1$ accompanied by the relation $\tau_c \sim q^{-1}$ which
33 matches the general behaviour of PNIPAm hydrogels. In accordance with literature^{9,12,18,57}
34 and the $I(q)$ showing indications of a transition from repulsive to attractive forces in regime
35 C the results point out the formation of a colloidal gel at high temperatures. This shows that
36 during heating this colloidal system undergoes a phase transition from a polymer-dominated
37 liquid where the structural relaxation process speeds up on raising the temperature until it
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rapidly turns into a jammed colloidal gel state.

Experimental Methods

Silica-PNIPAm core-shell nanoparticles were synthesized as explained in⁵⁸ and concentrated to a desired mass fraction. For the experiment the sample solution was filled in quartz capillaries with diameters of 1 mm and vacuum-sealed. To determine the size of both the uncoated silica and the silica-PNIPAm particles, DLS experiments have been performed at a 3D-DLS spectrometer-goniometer-system (LS Instruments AG, Switzerland). The particle size and hence the swelling-deswelling behaviour was analysed as a function of temperature. To prevent inter-particle interactions the concentration of silica-PNIPAm in H₂O was kept dilute with a weight fraction of $w < 0.2$ wt%.

XPCS measurements have been performed at the coherence beamline 8-ID-I of the Advanced Photon Source (APS) at the Argonne National Laboratory (USA) in small-angle X-ray-scattering (SAXS) geometry with a photon energy of 7.4 keV and a sample-detector distance of 4.0 m. The capillaries were mounted in a SAXS chamber with adjustable temperature. Samples were prepared at a mass fraction of $w = 14.6$ wt% which relates to a volume fraction of $\phi \approx 9.6$ Vol% in the fully collapsed state. The colloidal suspensions were measured between 15°C and 45°C with one degree steps around the LCST literature value of 32°C.³³ After reaching the desired temperature, an equilibration time of 600 s has been added before the speckle patterns have been measured. The X-ray beam was collimated to a size of $20 \times 20 \mu\text{m}^2$. The scattered intensity was measured with a two dimensional LAMBDA 750K (Large Area Medipix Based Detector Array) detector.⁵⁹ This high speed detector enables a deadtime-free readout up to a frame rate of 2 kHz with a counter depth of 12 bits which is crucial for measuring fast dynamical processes in the sample. Since PNIPAm is highly radiation sensitive the total dose has to be limited. With this requirement an exposure time of 0.5 ms per speckle pattern has been chosen with a series of 4000 diffraction

patterns at at least 15 different spots on the sample per temperature. Therewith the total illumination time can be associated with a dose $D \approx 1.5 \times 10^4$ Gy per spot which is below the radiation damage threshold of silica-PNIPAm.⁶⁰ As we did not observe any significant difference between different XPCS runs at a certain temperature, the g_2 -functions have been averaged to increase the statistical accuracy. Consequently, we did not observe any indication of aging during this period. Followed by the heating cycle, we performed measurements at different temperatures during cooling, indicating a fully reversible transition of structure and dynamics as observed for low concentrations.⁵⁸

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