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The Phase Diagram of Colloidal Silica-PNIPAm core-shell Nanogels

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We study structure and dynamics of aqueous dispersions of densely packed core-shell nanoparticles composed of a silica core and a poly(N-isopropylacrylamide) (PNIPAm) shell as a function of temperature and concentration. With small angle X-ray Scattering (SAXS) and X-ray photon correlation spectroscopy (XPCS) we shed light to the structural and dynamical changes of the thermo-responsive colloidal nanogel during its volume phase transition at a lower critical solution temperature (LCST) of 32°C. A transition of dynamics and its distinct dependency on the particle number concentration could be determined by analysing the intensity autocorrelation function while the structural transition remains concentration independent. We found the dynamics of a jammed system beyond a critical concentration. In addition, by variation of the PNIPAm shell size we tuned both the effective volume fraction and the underlying nature of the dynamics in the system. With our results we can present a full phase diagram of a PNIPAm core-shell system that spans from diluted suspensions, where the system behaves like a liquid, to an effective volume fraction of more than ninety percent where after exceeding a critical concentration the system undergoes a temperature-induced transition from a liquid towards a colloidal gel.

1 Introduction

Colloidal dispersions abound everywhere in daily life and offer numerous applications such as in paints, inks or pharmaceuticals. In particular, stimulus responsive cross-linked polymer networks as colloidal nanogels find increasing use in biomedicine and drug delivery^{1,2}. Aqueous poly(N-isopropylacrylamide) (PNIPAm) nanogels are a prominent and interesting system with a reversible volume phase transition at a so-called lower critical solution temperature (LCST) of 32°C³. Below this threshold temperature the nanogel particles are swollen due to hydrophilic water interaction while above the LCST the polymer network is hydrophobic. The result is a collapse of the particle volume by increase of the temperature where the stiffness of the collapsed particle increases significantly^{1,4-6}. With this property PNIPAm nanogel particles are particularly interesting for investigation of the phase transition and dynamics in soft colloidal systems. Numerous predominantly light scattering studies exist on the dynamics of PNIPAm hydrogels and micro- or nanogels in diluted suspensions⁷⁻¹². Investigations of dynamics in the technologically interesting dense-packed state when the samples are opaque

are, however, not accessible to dynamic light scattering (DLS) due to multiple scattering. Several studies on densely-packed PNIPAm systems revealed attractive inter-particle interaction above the LCST^{3,12,13} where the systems shows indications of gelation¹³⁻¹⁶. Below the LCST and at low particle concentrations, liquid and glass states have been identified. However, these rheology studies focused on mainly macroscopic properties of the samples, identifying e.g. the gelation transition. Insights on the structure and dynamics on the length scale of the particle size over a broad range of volume fractions are missing. The utilization of high-brilliance coherent X-rays paired with the latest detector generation enables the characterization of the nanoscopic structure and dynamics in both diluted and dense-packed colloidal systems¹⁷⁻²² and helps to acquire information on the full phase diagram of such thermo-responsive colloidal nanogels. To overcome the problem of low scattering contrast of an aqueous polymer we introduced strongly scattering silica nanoparticles as a core and covered it with a PNIPAm shell, without influencing the thermal response of the nanogel. In a previous XPCS study on dense-packed silica-PNIPAm nanogels we found structural and dynamical changes in the system around the LCST²³. The results show a transition in the system's dynamics upon heating composed of a speed-up followed by a rapid slow down at 37°C once the PNIPAm shell is fully collapsed. During the slow down, we found a second dynamical process. By analysing the intensity-intensity

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correlation function a transition from stretched to compressed exponential behaviour could be determined as the temperature is increased. Together with the respective dependency of the characteristic relaxation time on the wave vector transfer q the results reveal a transition from swollen repulsive particles²⁴ with polymer driven dynamics at lower temperatures towards a colloidal gel composed of collapsed attractive particles within one heating process^{11,12,25}. In contrast to the rheology studies^{13–16}, we observed intermediate states between the colloidal liquid at low temperature and the colloidal gel above 37°C suggesting a complex gelation process on the length scale of the particle size. To shed more light on this gelation process, knowledge of the phase behaviour over a broad range of volume fractions is needed.

In the present study we shed more light to the origin and dependencies of this temperature-induced transition of dynamics and investigate its reversibility. Intensity correlation functions from silica-PNIPAm nanogels at various concentrations and with different PNIPAm shell sizes provide information about their influence on the dynamical anomalies upon heating and cooling. These results enable the determination of a full phase diagram of silica-PNIPAm particles. It spans from diluted suspensions to an effective volume fraction of more than ninety percent and covers the full relevant temperature range around the LCST wherein we found liquid phases, a transition region with structural rearrangement and a jammed gel phase. While previous work mainly focused on the change of the interaction potentials our experimental results present the consequence for structure and dynamics of dense systems which are largely unexplored so far.

2 Materials and Methods

2.1 Silica-PNIPAm Synthesis

For the cores, silica nanoparticles were synthesized following the well-known Stöber method²⁶. The surface of the particles was functionalized with 3-(Trimethoxysilyl)propyl methacrylate (TPM) and afterwards grafted with PNIPAm. The PNIPAm shell was synthesized via free radical emulsion polymerization from N-isopropylacrylamide (NIPAm) monomers. For this process the surfactant sodium dodecyl sulfate (SDS), sodium sulfite Na_2SO_3 and water were added to the silica nanoparticle dispersion. Oxygen was removed by stirring the mixture for one hour under nitrogen flow at 60°C. Afterwards potassium peroxy disulfate ($\text{K}_2\text{S}_2\text{O}_8$) and ammonium iron(II) sulfate were added to initialize the polymerization process at 60°C by forming a redox couple. In the next step methylene bisacrylamide (BIS) and NIPAm, dissolved in ethanol, were added slowly. After the reaction has been fully completed the solution was filtered and dialyzed for one week in ultrapure water to remove the SDS²⁷. By using different amounts of BIS and NIPAm three different shell sizes have been synthesized on silica particles from the same stock dispersion. To obtain the same cross-linking density for all samples, the proportion between BIS and NIPAm was always kept constant. Following this procedure two silica batches have been synthesized and coated with PNIPAm. Table 1 shows all samples related to the subsequently presented data. Sample SP₁ has a swollen PNIPAm shell of 35 nm on a silica core of $R_{\text{Hsi}} = 50$ nm. For the second silica

Table 1 Hydrodynamic radii R_{H} of all samples measured by DLS. The respective swollen radius relates to $T = 20^\circ\text{C}$, the collapsed radius to $T = 45^\circ\text{C}$. $\Phi_{\text{eff},20}$ is the effective volume fraction of the samples studied by XPCS which is calculated using the particle size at 20°C .

Sample	R_{Hcore}	$R_{\text{Htotal}} (20^\circ\text{C})$	$R_{\text{Htotal}} (45^\circ\text{C})$	$\Phi_{\text{eff},20}$
SP ₁	50 nm	100 nm	75 nm	0.12 0.15 0.18
SP _{2A}	54 nm	76 nm	59 nm	0.13
SP _{2B}	54 nm	125 nm	70 nm	0.55
SP _{2C}	54 nm	220 nm	100 nm	0.73

batch with $R_{\text{Hsi}} = 54$ nm three different layer thicknesses have been synthesized. The shells were varied between the samples SP_{2A} with $R_{\text{Hsi}} \approx 20$ nm, SP_{2B} with $R_{\text{Hsi}} \approx 75$ nm and SP_{2C} with $R_{\text{Hsi}} \approx 140$ nm all in the swollen state at 20°C . With the known layer thickness in both the swollen and collapsed state the effective volume fraction $\Phi_{\text{eff},20}$ was calculated for each system at 20°C ¹⁰.

All samples were equally pre-characterized by DLS (see section 2.2) and consecutively studied by XPCS at several high concentrations. The sample suspensions were filled in borosilicate glass capillaries with diameters of 0.7 – 1 mm and vacuum-sealed.

2.2 Dynamic Light Scattering and X-ray Photon Correlation Spectroscopy

For the size characterization of the uncoated silica and the silica-PNIPAm particles and to ensure the reversible swelling-deswelling effect for single particles, DLS experiments have been performed at a 3D-DLS spectrometer-goniometer-system (LS Instruments AG, Switzerland). The instrument is built up with a 660-nm-wavelength HeNe-Laser and a temperature controllable sample environment with a precision of 0.1 K (Julabo Labortechnik GmbH, Germany). The particle size was analysed between 15°C and 50°C upon heating and subsequent cooling for a dilute aqueous silica-PNIPAm suspension with a weight fraction w of $w < 0.002$.

XPCS measurements have been performed at the coherence beamlines 8-ID-I of the Advanced Photon Source (APS, Lemont, USA) and ID10 of the European Synchrotron Radiation Facility (ESRF, Grenoble, France). The experimental setup conformed to a standard small-angle X-ray-scattering (SAXS) geometry with a photon energy of 7.4 keV, a sample-detector distance of 4.0 m and a collimated beam size of $20 \times 20 \mu\text{m}^2$ (8-ID-I) and a photon energy of 8.1 keV with a sample-detector distance of 5.3 m and a beam size of $10 \times 10 \mu\text{m}^2$ (ID10), respectively. At 8-ID-I the scattered intensity was measured with a two dimensional LAMBDA 750K (Large Area Medipix Based Detector Array) detector²⁸ containing 1536×512 pixels with a pixel size of $55 \times 55 \mu\text{m}^2$ each and a dead time free readout up to a frame rate of 2 kHz. In turn, at ID10 we used a MAXIPIX (Multichip Area X-ray detector based on a photon-counting Pixel array) 2×2 ²⁹ which achieves up to 300 Hz frame rate with 6 microseconds readout dead time containing 512×512 pixels with size of $55 \times 55 \mu\text{m}^2$.

With PNIPAm as a highly radiation sensitive sample system the

exposure of the sample to the X-ray beam had to be chosen carefully³⁰. After variation of attenuators, exposure times and beam sizes during the observation of the static and dynamic signal, exposure times between 0.5 ms and 3 ms per speckle pattern have been chosen with series of 500-4000 diffraction patterns at each sample spot. Within the chosen time scale any effect from beam damage could be avoided but the dynamics in the physically interesting time regime could still be determined. The total illumination time, *i.e.* the sum of all exposure times per series of diffraction patterns can be associated to a dose $D \approx 1.5 \times 10^4$ Gy which is below the radiation damage threshold for such silica-PNIPAm core shell systems³⁰. For longer exposure times per single diffraction pattern D was kept constant by means of attenuators.

Illumination of such a disordered colloidal system with coherent light creates a random speckled diffraction pattern $I(q, \tau)$ which changes with time according to the dynamics of the scattering objects^{17,21}. The dynamics in both DLS and XPCS experiments is given by the intensity-intensity autocorrelation functions

$$g_2(q, \tau) = \frac{\langle I(q, t) I(q, t + \tau) \rangle_t}{\langle I(q, t) \rangle_t^2} = 1 + \beta |f(q, \tau)|^2, \quad (1)$$

where $\langle \cdot \rangle$ is the temporal average over all times t . Therein, $I(q, t)$ represents the intensity at a certain wavevector transfer q and time t ³¹ whereas τ is the lagtime and $|q| = q = n \cdot \frac{4\pi}{\lambda} \sin \frac{2\theta}{2}$ with the refractive index n ($n \approx 1$ for X-rays³², $n \approx 1.33$ for $\lambda = 660$ nm), the wavelength of the incoming beam λ and the scattering angle 2θ . The right side of Eq. 1 contains the normalized intermediate scattering function $f(q, \tau)$ which is the fundamental quantity to describe the full time development of a colloidal suspension. For many soft matter systems the g_2 functions can be described by the Kohlrausch-Williams-Watts (KWW) function

$$g_2(q, \tau) = 1 + \beta \exp[-2(\Gamma(q) \cdot \tau)^\gamma] \quad (2)$$

where β is the speckle contrast, γ is the Kohlrausch exponent and $\Gamma(q)$ the relaxation rate which relates to the characteristic relaxation time τ_c via $\Gamma = \tau_c^{-1}$.

For soft matter systems, the relaxation time typically shows a certain q -dependency as $\tau_c \propto q^{-p}$. In case of diffusion the relaxation rate is given by $\Gamma(q) = D \cdot q^2$ with the (Stokes-Einstein) diffusion constant D ³³. Via the Stokes-Einstein relation the hydrodynamic radius R_H in DLS experiments is typically estimated as

$$R_H = q^{-2} \cdot \frac{k_B T}{6\pi\eta\Gamma}, \quad (3)$$

where η is the solvent viscosity (here H_2O).

3 Results

The static and dynamical behaviour of Silica-PNIPAm particles was studied for various core to shell ratios and concentrations. Sample SP₁ was prepared at mass fractions $w_1 = 0.07$, $w_2 = 0.09$ and $w_3 = 0.11$, which correspond to effective volume fractions of $\Phi_{\text{eff},20,1} = 0.12$, $\Phi_{\text{eff},20,2} = 0.15$, and $\Phi_{\text{eff},20,3} = 0.18$ (see Tab. 1). Measurements at all volume fractions were performed between 25°C and 40°C around the LCST literature value of 32°C³⁴ whereas beforehand the samples were equilibrated about 600 s

Fig. 1 SAXS results of SP₁: (a) $I(q)$ of silica-PNIPAm from top to bottom $\Phi_{\text{eff},20,1} = 0.12$, $\Phi_{\text{eff},20,2} = 0.15$ and $\Phi_{\text{eff},20,3} = 0.18$, respectively, measured between 25°C and 40°C. Intensity profiles have been shifted vertically for clarity. (b) Intensity $I(q_p)$ at a selected q value of $q_p = 0.042 \text{ nm}^{-1}$ as a function of temperature for all concentrations.

at each temperature. Sample SP₂ has been prepared with various shell thicknesses, denoted as SP_{2A}, SP_{2B} and SP_{2C} (see Table 1).

3.1 Static analysis

Fig. 1a shows the temperature dependence of the azimuthally and time-averaged intensity profile $I(q)$ obtained by SAXS of all three concentrations of SP₁, each upon heating from 25°C to 40°C. Here the main contribution to the scattering signal arises from the silica core with the first minimum of the form factor around $q = 0.1 \text{ nm}^{-1}$. While for all concentrations the $I(q)$ are almost identical for the lower three temperatures, they show a temperature and concentration dependence for temperatures higher than a threshold temperature T_c with $T_c \approx 36^\circ\text{C}$. For the upper temperatures $T > T_c$ all intensity profiles show an increase at low q values while a dip in intensity appears for approximately

$0.03 < q < 0.06 \text{ nm}^{-1}$ as it has been observed in our previous study²³. The effect is illustrated in Fig. 1b where the intensity at a selected q value of $q_p = 0.042 \text{ nm}^{-1}$ is shown for all $\Phi_{\text{eff},20}$ and T . With the profiles calibrated to $I(q_p)$ of $\Phi_{\text{eff},20,1}$ at $T = 25^\circ\text{C}$ the trend can be clearly identified as an effect of concentration whereby the decrease of $I(q_p)$ becomes more pronounced for higher concentrations.

Those changes in signal are attributed to the collapsing PNIPAm-shell and hence the appearance of attractive interactions between the particles³⁵. At low temperatures where the PNIPAm shells contain a large amount of water, van der Waals attractions between the particles can be neglected due to a close match of the dielectric constant of water and the PNIPAm shell. Furthermore, such soft sphere particles permit to be compressed in dense assemblies, which results in a repulsive short-range interaction potential. On the contrary, at high temperatures the shell is collapsed and hence the polymer density and stiffness increase around the core, leading to strong short-range attraction due to stronger van der Waals forces, hydrophobic effects and preferred polymer-polymer interactions^{3,25,36}. The change in $I(q)$ for $T \geq 36^\circ\text{C}$ hence suggests agglomerations, favourable due to deswelling of the PNIPAm shells with the ability to be deformed and/or inter-penetrated^{24,25}.

3.2 XPCS measurements

3.2.1 The influence of concentration on the transition of dynamics

In our previous study²³, a silica-PNIPAm suspension at $\Phi_{\text{eff},20} = 0.55$ with a core and shell size comparable to the one studied here showed a transition from sub-diffusive to hyper-diffusive dynamics upon heating. An initial speed up in the system while crossing the LCST is followed by a sudden slow down at $T \approx 37^\circ\text{C}$, which is accompanied by a second dynamical process visible in the double exponential decay of the g_2 function. The present study examines this effect as a function of temperature and concentration. For the XPCS experiments the scattering intensity and thus the accessible q range was limited due to the short exposure times on the sample. Fig. 2(a-f) shows the evolution of the intensity correlation functions g_2 with increasing temperature for $\Phi_{\text{eff},20} = 0.12, 0.15$ and 0.18 . All g_2 functions are shown at a selected q -value of 0.02 nm^{-1} with the corresponding KWW fit (Eq. 2, for q dependent g_2 functions see Fig. 1 in ESI). The speckle contrast β reflects the degree of coherence of the X-ray beam and is hence a setup dependent constant quantity. β was determined by measuring a static sample. At ID10 it was found to be $\beta_{\text{ID10}} \approx 0.3$, at 8-ID $\beta_{8\text{-ID}} \approx 0.15$.

Primarily, at all temperatures the correlation functions are shifted towards smaller timescales for lower $\Phi_{\text{eff},20}$, implying faster particle dynamics for lower concentrations. Furthermore, with increasing temperature from 25°C to 30°C and further to 32°C the g_2 functions show successively faster dynamics. Above 36°C no further development towards faster dynamics is present, however, the dynamical behaviour varies for each concentration upon further heating. While the g_2 functions of the system at $\Phi_{\text{eff},20,1} = 0.12$ remain unaffected and thus show no change in dy-

namics at 36°C , 38°C and 40°C , there is a clear slow down present in both higher concentrated samples. This temperature-induced transition of dynamics has been found to be a phase transition from a system with sub-diffusive dynamics of a liquid to a jammed colloidal gel with hyper-diffusive behaviour²³. The interaction of the system changes from a repulsive system²⁴ to an attractive colloidal gel^{11,12}.

The medium concentrated solution with $\Phi_{\text{eff},20,2} = 0.15$ shows a continuous slow-down between 36°C and 40°C . The KWW fit for the g_2 functions at 38°C and 40°C has been extended to a double exponential function

$$g_2(q, \tau) = 1 + (\beta - \alpha) \cdot \exp[-2(\Gamma_1(q) \cdot \tau)^\gamma] + \alpha \cdot \exp[-2(\Gamma_2(q) \cdot \tau)^\gamma], \quad (4)$$

where $\Gamma_1 = 1/\tau_{c1}$ and $\Gamma_2 = 1/\tau_{c2}$.

The contrast β was kept constant at 0.3 as for the single relaxation process, the pre-factor is $\alpha = 0.21$ for 38°C and $\alpha = 0.19$ for 40°C . In both cases the slower relaxation process does not fully decorrelate within the studied time range, nevertheless, the dynamics undergo a further change between 38 and 40°C . A clear decay of the g_2 function is present at 38°C while the process at 40°C shows no distinct decorrelation. The appearance of the second relaxation process indicates heterogeneous dynamics. This is usually present in glass formers or supercooled liquids³⁷⁻³⁹, during gel formation^{40,41} and have been also observed in our previous silica-PNIPAm study²³. For the highest concentration $\Phi_{\text{eff},20,3} = 0.18$ the g_2 functions of 38 and 40°C show no definitive decorrelation within the total exposure time. Hence, the system has become static in that time range.

Fig. 3(a) shows the development of all relaxation times with increasing temperature and Fig. 3(b) τ_c as a function of concentration. Similar to the static behaviour, the development of the characteristic relaxation time τ_c can be classified into two temperature regimes: For $T < T_C$ all relaxation times decrease linearly upon heating with larger relaxation times for higher concentrations (see inset Fig. 3a). Hence, the system speeds up independent of concentration upon heating from 25°C to 32°C with an initial relaxation time proportional to the particle concentration. From 36°C to 40°C and hence for $T > T_C$, τ_c shows a concentration dependent behaviour. While it remains constant for $\Phi_{\text{eff},20,1}$ the system with $\Phi_{\text{eff},20,3}$ does not decorrelate in the total experimental time of 1.5 s for $T = 38^\circ\text{C}$ and 40°C . Hence, no value of the relaxation time could be extracted, however, it is obvious that the relaxation time increases several orders of magnitude. Based on our previous results²³ and the outcome of the subsequently discussed experiment the KWW function with a compressed exponent of $\gamma = 2$ has been assumed for the g_2 functions which decorrelate about 1% in 1.5 s (for the temperature dependency of γ see Fig. 2 in ESI). This leads to a characteristic relaxation time of $\tau_c \approx 10$ s. In case of the sample with $\Phi_{\text{eff},20,1} = 0.12$ the compressed exponent indicates the slower relaxation process. The relaxation times obtained from the modelled KWW functions are shown in Fig. 3a with an error bar covering the wide range of potential values. As the g_2 function relating to $\Phi_{\text{eff},20,3}$ only drops

Fig. 2 Temporal evolution of the according correlation functions measured for $\Phi_{\text{eff},20,1} = 0.12$ (blue $\blacktriangle$), $\Phi_{\text{eff},20,2} = 0.15$ (green $\blacksquare$) and $\Phi_{\text{eff},20,3} = 0.18$ (yellow $\blacklozenge$) at (a) $T = 25^\circ\text{C}$, (b) $T = 30^\circ\text{C}$, (c) $T = 32^\circ\text{C}$, (d) $T = 36^\circ\text{C}$, (e) $T = 38^\circ\text{C}$ and (f) $T = 40^\circ\text{C}$. The g_2 functions were calculated at $q = 0.02 \text{ nm}^{-1}$, the solid lines represent the calculated fits. The temperature steps correspond to Fig. 1.

Fig. 3 (a) Temperature dependence of the characteristic relaxation time τ_c at $\Phi_{\text{eff},20,1} = 0.12$ (blue $\blacktriangle$), $\Phi_{\text{eff},20,2} = 0.15$ (green $\blacksquare$) and $\Phi_{\text{eff},20,3} = 0.18$ (yellow $\blacklozenge$). The inset depicts a zoom of the lower temperatures whereas the solid lines are guides to the eye. (b) Concentration dependence of τ_c of the swollen particle at 25°C (blue $\blacktriangleright$) and the collapsed particle at 38°C (red $\bullet$ τ_{c1} / $\circ$ τ_{c2}). All values correspond to the g_2 functions at $q = 0.02 \text{ nm}^{-1}$ presented in Fig. 2.

by 1% at $T = 45^\circ\text{C}$, τ_c is not modelled for this temperature. For the $\Phi_{\text{eff},20,2}$ sample whose g_2 function showed two dynamical processes τ_c is split up at high T . While τ_{c1} coincides with the decay observed for $\Phi_{\text{eff},20,1}$, τ_{c2} rises analogously to the highest concentration $\Phi_{\text{eff},20,3}$. The temperatures showing concentration-dependence and independence of the dynamic behaviour match with the temperatures found in the $I(q)$ (Fig. 1b).

Fig. 3b shows a different representation of the results in Fig. 3a with the relaxation time as a function of concentration. At 25°C the particles are swollen and τ_c hardly increases with concentration whereas we find a strong increase at 38°C where the particles are collapsed. This rapid deceleration has found to be accompanied by a transition from sub-diffusive to hyper-diffusive dynamics²³. Based on the presented results the transition of dynamics upon heating as well as the appearance of a second relaxation process can be interpreted as an effect of high particle concentration. Both effects are not present in more diluted systems and appear once a certain critical concentration is exceeded. While the static analysis showed the same transition from repulsive to attractive forces at high temperatures for all three concentrations the respective dynamic evolution towards higher temperatures clearly shows three different states. With the ability of fuzzy soft spheres to overlap and be deformed in densely packed assemblies^{25,42}, agglomerations due to the collapsed shells are favoured. Furthermore, the appearing inter-particle attraction facilitate the formation of colloidal gels^{36,41}. Both effects intensify with concentration and hence influence the corresponding

Fig. 4 Temperature dependent intensity correlation functions g_2 at $q = 0.02 \text{ nm}^{-1}$ for the respective lowest studied concentration with a swollen PNIPAm shell thickness of (a) 22 nm at $\Phi_{\text{eff},20}(\text{SP}_{2A}) \approx 0.13$, (b) 71 nm at $\Phi_{\text{eff},20}(\text{SP}_{2B}) \approx 0.55$ and (c) 186 nm at $\Phi_{\text{eff},20}(\text{SP}_{2C}) \approx 0.73$.

dynamics.

3.2.2 Variation of PNIPAm layer thickness

In addition, the effective volume fraction $\Phi_{\text{eff},20}$ was changed by variation of the PNIPAm layer thickness while keeping the core size constant. Therefore three different shell sizes have been grafted on silica cores from the same batch resulting in SP_{2A} with the smallest shell of 22 nm, SP_{2B} with a medium shell of 71 nm and SP_{2C} with the largest shell of 186 nm (in each case for $T = 20^\circ\text{C}$, see Table 1). With these three samples we cover a wide range of Φ_{eff} with $\Phi_{\text{eff},20}(\text{SP}_{2A}) \approx 0.13$, $\Phi_{\text{eff},20}(\text{SP}_{2B}) \approx 0.55$ and $\Phi_{\text{eff},20}(\text{SP}_{2C}) \approx 0.73$.

Fig. 4a-c shows the respective normalized intensity correlation functions including KWW fits as a function of temperature at $q = 0.02 \text{ nm}^{-1}$. While the temperature-dependent dynamics of SP_{2B} (Fig. 4b) have been discussed in detail in a previous study²³ we now classify it within a larger frame. We found that the dynamics of all three samples first becomes faster with increasing temperature between 36–38°C, until it rapidly slows down with further heating. Despite the common features the observed dynamics of each sample shows different characteristics. Sample SP_{2A} (Fig. 4a) shows the fastest dynamics of all three samples.

Fig. 5 (a) Temperature dependence of characteristic relaxation time τ_c for the lowest studied concentration of SP_{2A} (orange $\blacktriangle/\triangle$), SP_{2B} (pink $\blacktriangleleft$) and SP_{2C} (blue $\blacktriangledown$). Open symbols represent a second dynamical process at the respective temperature. (b) τ_c of variously concentrated silica-PNIPAm suspensions of SP_{2A} , SP_{2B} and SP_{2C} . All parameters correspond to the g_2 functions obtained at $q = 0.02 \text{ nm}^{-1}$ shown in Fig. 4, dashed lines represent guides to the eye.

All g_2 functions before the slow-down show a Kohlrausch exponent of $\gamma \approx 1$ which corresponds to diffusive motion in the regime. The slowing down occurs for $T > 38^\circ\text{C}$ and within a larger temperature interval than observed earlier for larger shell sizes. At the same time a second relaxation process occurs for 40°C and 42°C before it does no longer show any distinct time dependence at 45°C.

In comparison, the correlation functions of SP_{2B} (Fig. 4b) with the medium shell size are shifted towards larger times and hence related to slower particle motions than SP_{2A} . The dynamics become faster upon heating until 38°C while the slope of the g_2 functions with a stretched Kohlrausch exponent of $\gamma \approx 0.7$ indicates a change towards sub-diffusive dynamics for a higher shell thickness. For 40–45°C the sample becomes completely static within the studied time range.

Sample SP_{2C} with the largest shell size of 186 nm shows the slowest dynamics of all three SP_2 samples (Fig. 4c). Analogous to the other samples the g_2 functions show a speed up until 36°C followed by a rapid slow down until there is no apparent decorrelation for 40–45°C where the shell is fully collapsed. In this third case the Kohlrausch exponent is found to be $\gamma \approx 0.5$ pointing out a further shift towards sub-diffusive dynamics.

The direct comparison of Fig. 4 a-c hence clarifies the influence of the PNIPAm shell thickness on the dynamics in the system. Primarily, the particular set of g_2 functions for each sample was shifted to larger characteristic relaxation times with larger shell thicknesses. Furthermore, towards larger particles the slope of the correlation functions changed from a single exponential decay with $\gamma = 1$ to a stretched exponential decay with $\gamma = 0.5$ indicating a transition from diffusive motion for thin shells towards sub-diffusive motion for thicker PNIPAm shells. Fig. 5a gives a closer insight in the overall behaviour of τ_c with increasing temperature for all three shell sizes.

As before, we classify the threshold temperature T_c . For $T < T_c$, all three samples show a decrease of τ_c and hence a speed up in the system upon heating whereas we find slower dynamics for larger shell sizes.

For $T > T_c$ the characteristic relaxation time is found to be in the same regime, whereas the transition of τ_c passing T_c shows

a shell size dependent behaviour. For SP_{2A} the transition of dynamics happens between $T = 36^\circ\text{C}$ and $T = 38^\circ\text{C}$ where τ_c starts to increase until it raises more than four orders of magnitude at $T = 45^\circ\text{C}$. For $T = 42^\circ\text{C}$ τ_{c1} and τ_{c2} of both relaxation processes are plotted in Fig. 5.

Sample SP_{2B} shows a further decrease of τ_c by 32% at 36°C and before we see two slower relaxation processes at 37°C with $\tau_{c1} \approx 0.035\text{ s}$ matching with the relaxation time found for 34°C and $\tau_{c2} \approx 6.4\text{ s}$ increased by more than two orders of magnitude. Upon heating to 45°C τ_c shows a further tendency towards larger times. SP_{2C} initially shows a decrease of τ_c to 0.06 s at 36°C before it rises and stays constant around 4.9 s for $T \geq 38^\circ\text{C}$ which is in the same order of magnitude as the values obtained at low temperatures. While the transition at T_C clearly differs from both SP_{2A} and SP_{2B} whose characteristic relaxation times increase by several orders of magnitude, all τ_c match each other for $T > T_C$.

Additionally, we studied the dependence of τ_c on shell size and concentration, where each sample was prepared at different volume fractions. Fig. 5b shows τ_c of SP_{2A}, SP_{2B} and SP_{2C} at various $\Phi_{\text{eff},20}$ obtained at $T = 32^\circ\text{C}$ all for $q = 0.02\text{ nm}^{-1}$. For sample SP_{2C} with the largest shell thickness, large packing fractions lead to over-packed volumes with an effective volume fraction of $\Phi_{\text{eff},20} > 1^{42}$. The soft nanogel particles can be deformed, compressed and interpolate at high packing fractions which enables over-packed states due to reduction of the effective particle radius and hence of the actual volume fraction^{24,25,30,43}. Since we studied specifically high concentrations, representative parameters of the dynamics can only be shown for temperatures $T < T_C$ before the shell is collapsed. The graph shows both the rise in magnitudes of τ_c with larger shell sizes and $\Phi_{\text{eff},20}$ (for information about the temperature-dependency of R_H and $\Phi_{\text{eff},20}$ see Fig. 3 in ESI).

3.2.3 Reversibility

In order to study the reversibility of the volume phase transition and the previously described transition of dynamics present in highly concentrated silica-PNIPAm systems DLS and XPCS measurements have been performed both upon heating from 15°C to 45°C and with subsequent stepwise cooling down to 15°C . Fig. 6a shows the hydrodynamic radius of SP₁ as a function of temperature obtained by DLS. As mentioned above the particles collapse from an initial $R_H \approx 100\text{ nm}$ at 15°C to $R_H \approx 75\text{ nm}$ at 45°C while crossing the LCST. The subsequent cooling reverses the behaviour whereby the radius increases. The deswelling and swelling processes match each other without indications of a hysteresis which shows that the temperature induced modification of hydrophilicity of the PNIPAm shell is completely reversible. The reversibility of the transition of dynamics in highly concentrated systems was determined with the earlier discussed sample system SP₁ at $\Phi_{\text{eff},20} = 0.18$ (see Fig. 2) in a separate temperature dependent XPCS experiment. Fig. 6b shows the overall behaviour of the characteristic relaxation time upon heating and cooling. To obtain representative results of τ_c in the slow regime at high temperatures XPCS measurements have been additionally performed with an exposure time of 5 ms and a series of 2000 diffraction patterns keeping the same dose by using attenuators. With a total

Fig. 6 Temperature dependence of (a) the hydrodynamic radius R_H of SP₁ characterized by DLS upon heating (red *) and cooling (blue □), (b) τ_c of SP₁ at $\Phi_{\text{eff},20} = 0.18$ (see Fig. 2 and Fig. 3a) and (c) the corresponding $I(q)$ for $T = 25^\circ\text{C}$, 36°C and 45°C in bidirectional manner. The arrow indicates the sequence of the measurements. All data was taken upon heating and subsequent cooling. The dashed lines in (a) and (b) represent guides to the eye.

exposure time of 10 s and the result from our previous study²³ the KWW function with $\gamma \approx 2$ was adapted to the data. The result shows an accelerating τ_c between 15°C and 37°C before the value rises by three orders of magnitude as previously observed and shown in Fig. 3a. The cooling process shows a reversed behaviour with a drop in τ_c . In contrast to the dilute case (Fig. 6a) a small hysteresis can be identified between 38°C and 40°C . The comparison of Fig. 6a and b clarifies the occurrence of the transition of dynamics once the PNIPAm shell is fully collapsed at $T \approx 36^\circ\text{C} = T_C$. Furthermore, reversibility was also found in the $I(q)$ (Fig. 6c). The feature due to the collapsing PNIPAm shell appearing in $I(q)$ for $36^\circ\text{C} < T < 45^\circ\text{C}$ (see. Fig. 1) disappears with decrease of temperature. Hence, the attractive inter-particle potential of the collapsed system^{11,12,23} changes back into repulsion between the fully re-swollen particles. The results show clear reversibility of both the temperature induced static and dynamical phase transition.

3.2.4 Phase Diagram

All our results discussed here and in ref. 23 together with additional data can be assembled in a phase diagram of silica-PNIPAm as a function of temperature and concentration in the representation of the effective volume fraction Φ_{eff} calculated for the respective temperature (Fig. 7).

We find a fluid phase (blue ○) for $T < \text{LCST}$ as well as for low Φ_{eff} where the dynamics speed-up monotonously with increasing temperature. The g_2 functions show diffusive dynamics with $\gamma \approx 1$ for dilute suspensions and subdiffusive dynamics with $\gamma \approx 0.5$ at higher concentrations, both with $p \geq 2$. The $I(q)$ shows no indications for agglomeration, suggesting repulsive interactions (cf. section 3.1). Systems with very low Φ_{eff} remain in this phase independent of temperature. For medium to high Φ_{eff} and $\text{LCST} < T < T_C$ a fast fluid phase is defined (orange △). Here,

Fig. 7 Phase diagram of silica-PNIPAm in the effective volume fraction Φ_{eff} -temperature T representation. Each symbol represents a performed measurement. The blue circles ($\circ$) denote the region where the system behaves like a fluid. In the green region ($\diamond$) the g_2 functions show two relaxation processes associated with a structural rearrangement in the system. The neighbouring orange regime ($\triangle$) relates to a rapid speed up of the particles. In the red regime (∇) the particles form a colloidal gel. The horizontal dashed line indicates the LCST at 32°C.

τ_c decreases rapidly compared to the fluid phase. With increasing temperature the value of γ increases with $0.5 < \gamma < 1$ (for information about the temperature-dependency of p and γ see Fig. 4 in ESI). The $I(q)$ are still temperature-independent in this regime. In the rearrangement phase (green $\diamond$) for medium concentrations and $T \approx T_C$ the g_2 functions show two relaxation processes. The overall dynamics in this regime is slower compared to the liquid phases. The $I(q)$ show indications of the appearance of attractive forces in the system (cf. section 3.1). At high temperatures $T > T_C$ this matches a colloidal gel phase (red ∇)^{3,13–16}. Here, τ_c increases several orders of magnitude compared to the fluid phases. The system shows the dynamics of a colloidal gel with a KWW exponent $\gamma > 1$ and $p \approx 1$. In this phase the $I(q)$ suggest stronger attraction with increasing temperature.

We find the fluid phase to be dominating where the colloidal suspension behaves like a liquid. Remarkably, we observed such fluid-like dynamics over the whole range of volume fractions studied for $T < \text{LCST}$. At $T > 32^\circ\text{C}$ a phase boundary occurs for $\Phi_{\text{eff}} \gtrsim 0.1$. The medium concentrations such as SP₁ at $\Phi_{\text{eff}} = 0.15$, SP_{2A} and SP_{2B} show a structural rearrangement expressed by a slow down accompanied with a second relaxation process whereas all $\Phi_{\text{eff}} \gtrsim 0.32$ show a further rapid increase of τ_c up to $T \approx 36^\circ\text{C}$. In the high-temperature regime the characteristic relaxation times of all $\Phi_{\text{eff}} \gtrsim 0.1$ increase by several orders of magnitude and show the dynamics of a colloidal gel as observed for SP₁ at $\Phi_{\text{eff}} = 0.18$ and SP_{2B}²³.

Overall, the phase diagram clarifies the possibility to achieve a transition from a liquid to a colloidal gel phase within one heating process. In contrast to the observation of a transition in PNIPAm microgels from a jammed glassy to a fluid state by heating up

to the LCST¹³ we found that all our systems behave like a fluid in the regime of $T < \text{LCST}$ and have no indications for jamming or crystallization related to a critical packing fraction as reported elsewhere^{44–47}.

4 Conclusions

In conclusion, we investigated the temperature-induced transition of structure and dynamics of densely packed silica-PNIPAm core-shell systems using XPCS. This transition was found to be concentration dependent. By systematic dilution of a highly concentrated system this transition could be tuned. With the particular characteristic relaxation time the dynamics of all studied concentrations could be classified in two temperature intervals, defined by a critical temperature T_C . Below T_C all concentrations show an acceleration of the observed particle motion upon heating where slower dynamics is observed for higher concentrations. In contrast, for $T > T_C$ the corresponding behaviour varies with concentration. In this study, the highest concentration of $\Phi_{\text{eff}} = 0.18$ shows a slow down which is consistent with our previous study²³, whereas no further change in dynamics is present upon heating of the most diluted solution of $\Phi_{\text{eff}} = 0.12$. For the medium concentration with $\Phi_{\text{eff}} = 0.15$ two relaxation processes appear $T > T_C$ with a fast process matching the dynamics of the lowest concentration and a slow process analogue to the highest concentration. On the contrary to those three different states in the overall dynamical behaviour the structural analysis shows a transition from repulsive to attractive forces as a result of the collapsing shell for all three concentrations. The attractive interparticle interactions paired with the dynamic slow-down suggests colloidal gel formation in the dispersion once the particle shells are collapsed. Both effects are more pronounced for dense particle packings and influence the dynamics leading to its transition with a structural relaxation time in the range of $\tau_c \approx 10$ s.

Additionally, the original PNIPAm shell thickness has a clear influence on particle motion before the transition of dynamics occurs. While particles with a shell thickness of 10 nm show diffusive behaviour with the Kohlrausch exponent of $\gamma = 1$, the g_2 functions become stretched for thicker shells and thus show a shift towards sub-diffusive dynamics with $\gamma < 1$. Here the critical transition temperature is independent of the PNIPAm shell size. For the sample with the thinnest shell the process of the transition of dynamics occurs over a wide range of temperature steps between 36°C and 42°C whereas the two larger shells show a sudden slow down within the temperature step of one degree. The alluded temperature-dependent transition of structure and dynamics in highly concentrated systems as well as the particle size was demonstrated to be fully reversible with increase and subsequent reduction of the temperature in a broad range around the LCST. Within this a dynamical hysteresis has been found for concentrated systems. Based on all results we can present a phase diagram with the overall temperature- and concentration dependence of silica-PNIPAm particles for the first time. It separates two different fluid states from a rearrangement phase and the jammed state at high packing fractions and temperatures where the system forms a colloidal gel. In comparison to studies on pure PNIPAm microgels no crystal formation was present at any Φ_{eff} or

temperature.

Conflicts of interest

There are no conflicts to declare.

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Notes and references

- M. Das, H. Zhang and E. Kumacheva, *Annu. Rev. Mater. Res.*, 2006, **36**, 117–142.
- Y. Guan and Y. Zhang, *Soft Matter*, 2011, **7**, 6375–6384.
- P. J. Yunker, K. Chen, M. D. Gratale, M. A. Lohr, T. Still and A. G. Yodh, *Rep. Prog. Phys.*, 2014, **77**, 056601.
- K. László, A. Fluerasu, A. Moussaïd and E. Geissler, *Soft Matter*, 2010, **6**, 4335–4338.
- S. A. Deshmukh, S. K. Sankaranarayanan, K. Suthar and D. C. Mancini, *J. Phys. Chem. B*, 2012, **116**, 2651–2663.
- S. M. Hashmi and E. R. Dufresne, *Soft Matter*, 2009, **5**, 3682–3688.
- J. Wang, D. Gan, L. A. Lyon and M. A. El-Sayed, *J. Am. Chem. Soc.*, 2001, **123**, 11284–11289.
- R. Hernández, M. Criado, A. Nogales, M. Sprung, C. Mijangos and T. A. Ezquerro, *Macromolecules*, 2015, **48**, 393–399.
- P. Holmqvist, P. Mohanty, G. Nägele, P. Schurtenberger and M. Heinen, *Phys. Rev. Lett.*, 2012, **109**, 048302.
- Q. Li, X. Peng and G. B. McKenna, *Soft Matter*, 2019, **15**, 2336–2347.
- A. Zacccone, J. J. Crassous, B. Béri and M. Ballauff, *Phys. Rev. Lett.*, 2011, **107**, 168303.
- A. Zacccone, J. J. Crassous and M. Ballauff, *J. Chem. Phys.*, 2013, **138**, 104908.
- G. Romeo, A. Fernandez-Nieves, H. M. Wyss, D. Acierno and D. A. Weitz, *Adv. Mater.*, 2010, **22**, 3441–3445.
- J. Appel, B. Fölker and J. Sprakel, *Soft Matter*, 2016, **12**, 2515–2522.
- J. Appel, N. de Lange, H. M. van der Kooij, T. van de Laar, J. B. ten Hove, T. E. Kodger and J. Sprakel, *Part. & Part. Syst. Char.*, 2015, **32**, 764–770.
- A. Town, E. Niezabitowska, J. Kavanagh, M. Barrow, V. R. Kearns, E. García-Tuñón and T. O. McDonald, *The Journal of Physical Chemistry B*, 2019, **123**, 6303–6313.
- G. Grübel, A. Madsen and A. Robert, in *Soft Matter Characterization*, Springer, 2008, pp. 953–995.
- O. G. Shpyrko, *J. Sync. Rad.*, 2014, **21**, 1057–1064.
- A. Madsen, A. Fluerasu and B. Ruta, *Synchrotron Light Sources and Free-Electron Lasers: Accelerator Physics, Instrumentation and Science Applications*, Springer, 2016, pp. 1617–1642.
- A. R. Sandy, Q. Zhang and L. B. Lurio, *Annual Review of Materials Research*, 2018, **48**, 167–190.
- G. Grübel and F. Zontone, *J. Alloys Compd.*, 2004, **362**, 3–11.
- A. Robert, J. Wagner, T. Autenrieth, W. Härtl and G. Grübel, *J. Magn. Magn. Mater.*, 2005, **289**, 47–49.
- L. Frenzel, F. Lehmkuhler, I. Lokteva, S. Narayanan, M. Sprung and G. Grübel, *J. Phys. Chem. Lett.*, 2019, 5231–5236.
- M. J. Bergman, N. Gnan, M. Obiols-Rabasa, J.-M. Meijer, L. Rovigatti, E. Zaccarelli and P. Schurtenberger, *Nat. Commun.*, 2018, **9**, 5039.
- P. S. Mohanty, S. Nöjd, K. van Grujthuijsen, J. J. Crassous, M. Obiols-Rabasa, R. Schweins, A. Stradner and P. Schurtenberger, *Sci. Rep.*, 2017, **7**, 1487.
- W. Stöber, A. Fink and E. Bohn, *J. Colloid Interface Sci.*, 1968, **26**, 62–69.
- N. Nun, S. Hinrichs, M. A. Schroer, D. Sheyfer, G. Grübel and B. Fischer, *Gels*, 2017, **3**, 34.
- D. Pennicard, S. Lange, S. Smoljanin, J. Becker, H. Hirsemann, M. Epple and H. Graafsma, *J. Instrum.*, 2011, **6**, C11009.
- C. Ponchut, J. Rigal, J. Clément, E. Papillon, A. Homs and S. Petitdemange, *J. Instrum.*, 2011, **6**, C01069.
- F. Lehmkuhler, J. Valerio, D. Sheyfer, W. Roseker, M. A. Schroer, B. Fischer, K. Tono, M. Yabashi, T. Ishikawa and G. Grübel, *IUCrJ*, 2018, **5**, 801–807.
- B. J. Berne and R. Pecora, *Dynamic light scattering: with applications to chemistry, biology, and physics*, Courier Corporation, 1976.
- J. Als-Nielsen and D. McMorrow, *Elements of modern X-ray physics*, John Wiley & Sons, 2011.
- S. Dierker, R. Pindak, R. Fleming, I. Robinson and L. Berman, *Phys. Rev. Lett.*, 1995, **75**, 449.
- C. Wu and X. Wang, *Phys. Rev. Lett.*, 1998, **80**, 4092.
- T. Narayanan, M. Sztucki, G. Belina and F. Pignon, *Phys. Rev. Lett.*, 2006, **96**, 258301.
- J. Wu, B. Zhou and Z. Hu, *Phys. Rev. Lett.*, 2003, **90**, 048304.
- S. Capaccioli, M. Paluch, D. Prevosto, L.-M. Wang and K. Ngai, *J. Phys. Chem. Lett.*, 2012, **3**, 735–743.
- H. Tanaka, *Phys. Rev. E*, 2004, **69**, 021502.
- P. G. Debenedetti and F. H. Stillinger, *Nature*, 2001, **410**, 259.
- Q. Zhang, D. Bahadur, E. M. Dufresne, P. Grybos, P. Kmon, R. L. Leheny, P. Maj, S. Narayanan, R. Szczygiel, S. Ramakrishnan *et al.*, *Phys. Rev. Lett.*, 2017, **119**, 178006.
- H. Guo, S. Ramakrishnan, J. L. Harden and R. L. Leheny, *J. Chem. Phys.*, 2011, **135**, 154903.
- G. M. Conley, P. Aebischer, S. Nöjd, P. Schurtenberger and F. Scheffold, *Sci. Adv.*, 2017, **3**, e1700969.
- N. Gnan and E. Zaccarelli, *Nature Phys.*, 2019, **15**, 683–688.
- B. Sierra-Martin and A. Fernandez-Nieves, *Soft Matter*, 2012,

- 8, 4141.
- 45 H. Senff and W. Richtering, *J. Chem. Phys.*, 1999, **111**, 1705–1711.
- 46 R. Shu, W. Sun, Y. Liu, T. Wang, C. Wang, X. Liu and Z. Tong, *Colloids Surf., A*, 2013, **436**, 912–921.
- 47 A. N. S. John, V. Breedveld and L. A. Lyon, *J. Phys. Chem. B*, 2007, **111**, 7796–7801.