Glass-liquid and glass-gel transitions of soft-shell particles

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Abstract

We study the structure and dynamics of colloidal particles with a spherical hard core and a thermo-responsive soft shell over the whole phase diagram by means of small-angle X-ray scattering and X-ray photon correlation spectroscopy. By changing the effective volume fraction by temperature and particle concentration, liquid, repulsive glass and attractive gel phases are observed. The dynamics slow down with increasing volume fraction in the liquid phase and reflect a Vogel-Fulcher-Tamann behaviour known for fragile glass formers. We find a liquid-glass transition above 50 vol.% that is independent from the particles' concentration and temperature. In an over-packed state at effective volume fractions above 1, the dispersion does not show a liquid phase but undergoes a gel-glass transition at an effective volume fraction of 34 vol.%. At the same concentration, extrema of subdiffusive dynamics are found in the liquid phase at lower weight fractions. We interpret this as dynamic precursors of the glass-gel transition.

Upon supercooling the structural relaxation time of many liquids grows by orders of magnitude before they undergo a glass transition [1, 2]. In recent years, similar observations have been made for colloidal systems where the volume fraction of the particles defines the sample phase [3]. Due to its importance as a model system for theory and experiments, special attention has been paid to the hard-sphere glass transition [3–5]. With increasing volume fraction, structural order develops in hard sphere systems in the liquid state [6, 7]. Upon supercooling, i.e., above volume fractions of $\phi \approx 0.5$, the structural correlation time grows and diverges at the glass transition around $\phi_0 \approx 0.59$. This is described by a Vogel-Fulcher-Tamann (VFT) behaviour similar to other glass formers [1–3], where the relaxation time τ follows an exponential that diverges at a VFT volume fraction $\phi_{\text{VFT}} \geq \phi_0$

$$\tau \propto \exp \left(\frac{m\phi_0}{\phi_0 - \phi} \right). \quad (1)$$

The so-called fragility index m is a measure of the deviation from an Arrhenius-type behaviour of the viscosity or relaxation time while approaching the glass transition.

Recently, research has been extended to so-called soft colloidal systems that show a much richer phase behaviour, such as different crystalline states observed in dispersions of charged particles [8]. A special class of frequently studied soft particles are microgels or nanogels made from Poly(N-isopropylacrylamide) (PNIPAm). Such PNIPAm particles dispersed in

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water show a reversible volume phase transition at a lower critical solution temperature (LCST) of 306 K [9–13]. Below this LCST, the polymer is hydrophilic and the particles hence swollen with water. The interaction is typically described by a repulsive Hertzian potential [14, 15]. They become hydrophobic above this temperature, releasing the water and forming a collapsed state. Therefore, besides the volume fraction the phase of such a microgel dispersion depends on the temperature T as well. Above the LCST, the particles become attractive, promoting the formation of a colloidal gel at high volume fractions [16–27].

As the degree of swelling and thus the direct particle interaction varies with T , comparing PNIPAm systems at different temperatures is difficult, in particular using the temperature to change the volume fraction of the dispersion. Therefore, the glass transition of such dispersions has been studied typically at constant temperature, changing the volume fraction only [11, 12]. Several similarities between the glass transition of hard and soft spheres have been reported [28], however, many properties remain unclear or controversial, such as the fragility, the role of softness, and the relation to gelation and jamming transitions [28–44].

In this work we address the relation between the glass, gel and liquid phases by studying the structure and dynamics of colloidal soft spheres made from a hard spherical SiO_2 core and a soft PNIPAm shell by means of small-angle X-ray scattering (SAXS) and X-ray photon correlation spectroscopy (XPCS). By modifying the particle number density via the weight fraction and the particles radius by temperature changes between 288 K and 318 K effective volume fractions between $\zeta = 0.03$ and $\zeta = 1.6$ are reached, covering liquid, glass and gel phases. In the liquid phase, the sample dynamics slows down with increasing volume fraction following a Vogel-Fulcher-Tamann law. At $\zeta_0 = 0.51$, the dynamics falls out-of-equilibrium indicating a liquid-glass transition, independent of the particles’ weight fraction and temperature, and thus the interaction potential. At high weight fractions, overpacked states are reached at 288 K, i.e. $\zeta > 1$. In this case the system does not show a liquid phase and undergoes a gel-glass transition at $\zeta_{\text{gg}} = 0.34$. In the liquid phase at lower weight fractions extrema of subdiffusive dynamics are found at ζ_{gg} suggesting the existence of dynamic precursors of the glass-gel transition.

We study the structure and dynamics at weight fractions between $c = 4$ wt.% and 15.8 wt.% of silica-PNIPAm core-shell nanoparticles. Their hydrodynamic radius is 228 nm in the swollen state at 15°C and 100 nm in the collapsed state at 45°C. Details of the synthesis

of the nanoparticles and details of the XPCS experiment performed at beamline P10 at PETRA III (DESY, Hamburg, Germany) are given in the Supplementary Materials.

In dynamic light scattering (DLS) and XPCS experiments the dynamics of a sample are probed by auto-correlating the intensity $I(q, t)$ at time t and the modulus of the wave vector transfer $q \equiv |\mathbf{q}| = \frac{4\pi n}{\lambda} \sin(\theta/2)$. Here, n is the index of refraction which is ≈ 1 for X-rays, λ the wave length and θ the scattering angle. The correlation function is given by

$$g_2(q, \Delta t) = \frac{\langle I(q, t)I(q, t + \Delta t) \rangle_t}{\langle I(q, t) \rangle_t^2}. \quad (2)$$

For the samples studied here this g_2 -function can be expressed by the intermediate scattering function $f(q, \Delta t)$ that is given by a Kohlrausch-Williams-Watts (KWW) expression

$$g_2(q, \Delta t) = 1 + \beta |f(q, \Delta t)|^2 = 1 + \beta \exp(-2(\Gamma \Delta t)^\gamma). \quad (3)$$

The speckle contrast β is defined by coherence properties of the X-ray beam and setup parameters. It is close to 1 for DLS and was found to be 0.18 in the XPCS experiment.

The relaxation time τ is given by the inverse of the relaxation rate $\tau = \Gamma^{-1}$. The q -dependence of $\Gamma \propto q^p$ and the KWW-exponent γ typically define the type of dynamics, e.g., for diffusion of colloidal particles one obtains $\gamma = 1$ and $\Gamma(q) = D_0 q^2$, with the Stokes-Einstein diffusion coefficient $D_0 = \frac{k_B T}{6\pi\eta r}$. This is used in DLS experiments to obtain the particles' hydrodynamic radius r with Boltzmann's constant k_B , the known temperature T and solvent viscosity η .

As the PNIPAm particles deform and deswell at large volume fractions, an effective volume fraction is conventionally used defined by $\zeta = N \cdot V(T)$, with N the particle number concentration and $V(T)$ the volume fraction of a particle in a dilute dispersion at temperature T as obtained by dynamic light scattering [39, 45, 46]. Values around and above $\zeta = 1$ are possible with deformed particles and interpenetration of the PNIPAm shell [12, 13, 45, 47–50]. Depending on the softness of pure PNIPAm particles the real volume fraction matches ζ up to approximately $\zeta = 0.8$ [46, 51]. At higher volume fractions the particles are not in swelling equilibrium [31].

Intermediate scattering functions and fits of Eq. 3 to the data are exemplary shown for $c = 9$ wt.% at $T = 288$ K and $T = 313$ K in the Supplementary Material together with the temperature dependence of the so-obtained τ and the two exponents p and γ . Here, we discuss the results as a function of the effective volume fraction of all samples

studied. Since the radius of the core-shell particles shrinks already below the LCST, each experiment at a fixed weight fraction and temperature corresponds to a different effective volume fraction ζ . The relaxation time τ is shown in Fig. 1 (a) as a function of ζ . Despite of the different number densities and temperatures, the measured relaxation times τ seem to collapse on a common master curve. This is surprising because the interaction potential significantly changes with particle swelling and thus with temperature [15]. This may lead to different dynamics at different temperatures, especially below the LCST. Even above 311 K (open diamonds), where we recently reported gelation due to the appearance of attractive interaction between the particles [26], the data follows the trend for $c < 10$ wt.%. Samples at higher concentrations do not speed up as discussed in the Supplementary Material and eventually reach a gel phase.

In general, the slowing down with increasing ζ appears to resemble the behaviour of fragile glass formers reaching the glass transition [28, 52]. The relaxation time grows steeply up to $\zeta \approx 0.5$ and changes to a slower, linear growth above. We modelled the increase of τ for $\zeta \lesssim 0.5$ by a Vogel-Fulcher-Tamann (VFT) law

$$\tau(\zeta) = \tau_0 \exp \left(\frac{m\zeta_{\text{VFT}}}{\zeta_{\text{VFT}} - \zeta} \right) \quad (4)$$

where τ_0 is a scaling parameter, m the fragility index, and ζ_{VFT} is the VFT volume fraction where $\tau \rightarrow \infty$. We fitted Eq. 4 to our data for $0.0036 \text{ nm}^{-1} \leq q \leq 0.017 \text{ nm}^{-1}$ and $c \leq 9$ wt.% and obtained $\zeta_{\text{VFT}} = 0.84 \pm 0.03$ and an index of $m = 6.1 \pm 0.2$. In literature, using viscosity measurements broad range of ζ_{VFT} has been reported for different soft particle systems ranging from 0.5 to more than 1.2, mainly depending on the degree of softness [39, 53, 54]. Note that ζ_{VFT} found here matches results from pure PNIPAm microgels obtained by DLS [28].

In literature, different definitions of the fragility index are discussed. For instance, the kinetic fragility m^* defined as [29, 39, 44]

$$m^* = \left[\frac{\partial \log(\tau)}{\partial(\zeta/\zeta_g)} \right]_{\zeta=\zeta_g}, \quad (5)$$

uses a glass transition volume fraction ζ_g . Following the definition from Mattson et al. [29] we may fix the glass transition at $\tau/\tau_0 = 10^5$ and obtain $\zeta_g = 0.587$. This is close to the glass transition found for hard spheres [3, 39]. At this value we have $m^*(\zeta_g) = 1.2$. A different prominent choice of ζ_g in Eq. 5 is given by $\zeta_0 = 0.51$. Above ζ_0 the VFT fails to describe

FIG. 1. a) Relaxation time τ at $q = 0.0116 \text{ nm}^{-1}$ as function of volume fraction. Open diamonds correspond to $T \geq 311 \text{ K}$, full circles represent $T < 311 \text{ K}$. Solid black line is the fit of the VFT model, the empiric dashed line is a linear fit for high ζ and a power law for low ζ . The crossover of solid and dashed line is found at $\zeta_0 = 0.510$. b) Exponent p and c) exponent γ as function of volume fraction. Vertical dashed lines mark ζ_{gg} , ζ_0 , and ζ_{VFT} .

the data and we obtain $m^*(\zeta_0) = 0.93$. Both kinetic fragilities indicate that our core-shell sample is a strong glass former, supporting findings from previous studies on soft particles [29, 39, 44].

The behaviour for $\zeta > 0.5$ and in general for $c \geq 12 \text{ wt.}\%$ shown as dashed line in

Fig. 1 (a) was empirically modelled by the sum of a power law $\tau \propto \zeta^{-1.7}$ dominating at low volume fractions and a linear relation at high volume fractions. Such a power law behaviour has been reported for PNIPAm-based gels [20, 31]. The change from the power law to the linear behaviour is found at $\zeta_{gg} = 0.34$, the crossing of the linear fit and the VFT model is located at $\zeta_0 = 0.510$. In Fig. 1 (b) and (c) we show exponents p and γ . For $\zeta < \zeta_0$ and $c < 10$ wt.% we find $p \geq 2$ and $\gamma \leq 0.8$, which is typical for the liquid state [23, 26]. We find a maximum of p ($p_{\max} \approx 4$) that coincides with a minimum of the KWW exponent ($\gamma_{\min} \approx 0.6$). Remarkably, both extrema are located at ζ_{gg} obtained from the dynamics of the sample at high weight fractions. This may suggest the existence of a dynamic precursor of the glass-gel transition at the same ζ but lower weight fractions.

Above ζ_0 , the exponents agree to values obtained at lower volume fractions, i.e. $p = 2$ to 3 and $\gamma \approx 0.8$. This suggests that the sample is in a supercooled, liquid state with diffusive dynamics. Notably, the dynamics show similar behaviour reported from light scattering experiments on PNIPAm systems where the temperature was fixed and the volume fraction was changed by modification of the number density of PNIPAm particles [44]. For high weight fractions the exponents describe glassy states above ζ_0 with ballistic dynamics indicated by $p \approx 1$ and $\gamma > 1.5$. Similar to the relaxation time τ , both exponents of the two highest weight fractions only show weak modulations. In particular, $p \approx 1$ is found for all concentrations, while γ follows the same trend found for τ . This implies that these samples do not show a liquid state and stay in a glass or gel phase over the whole range of volume fractions studied.

The sample dynamics will now be compared to structural properties. Therefore, the structure factors $S(q, c, T)$ are calculated via $S(q, c, T) = I(q, c, T)/P(q, T)$, with the single particle form factors $P(q, T)$ measured from a dilute dispersion. The structure factors are shown in Fig. 2 (a)-(d) for four weight fractions. In general, all $S(q)$ show the same tendencies with changing temperatures. At low temperature, the first peak is found around $q = 0.02$ to 0.03 nm^{-1} where its position $q_{\max}$, reflecting the effective next-neighbour distance, and its height $S_{\max} = S(q_{\max})$ depend on the weight fraction. In addition, for $q \rightarrow 0$ the structure factors converge around $S(q \rightarrow 0) \approx 0.5$ to 0.6 .

With increasing temperature, the peak position shifts to larger q and the peak height decreases, indicating a reduced particles size and thus a reduced volume fraction and less-ordered next-neighbour shell. This is accompanied by a gradual increase of the contribution

FIG. 2. a)-d) Structure factors for selected weight fractions: a) 4 wt.%, b) 6.5 wt.%, c) 9 wt.%, d) 15.8 wt.%. e) Relative position Δq_{max} and f) height $S_{\text{max}} = S(q_{\text{max}})$ of the structure factor peak for all studied samples.

at $q \rightarrow 0$, especially for low weight fractions. In contrast, $S(q)$ for the sample at $c = 15.8$ wt.% shows only weak modifications up to 310 K, underlining the glass state at this weight fraction. Increasing the temperature above 310 K the structure factors show significant changes, in particular a strong increase at $q \rightarrow 0$ and thus a shift of q_{max} . The overall similarities of $S(q)$ at all concentrations prove the transition from repulsive interactions at low temperatures towards attractive interactions above the gelation temperature $T_{\text{gel}} = 310$ K as suggested previously for such core-shell systems [23, 26].

The values of q_{max} and S_{max} are shown in Fig. 2 (e) and (f) as a function of ζ . In fact, q_{max} depends on the weight fraction and thus shows slightly different values at similar volume fractions (see Supplementary Material). In order to compare the different weight fractions, we show difference values Δq_{max} with respect to $q_{\text{max}}(\zeta_0)$ at the respective weight fraction. These have been obtained by a fit to a power law at high volume fractions (see Supplementary Material). For $\zeta \gtrsim 0.15$ q_{max} slightly drops as discussed above. With decreasing volume fraction, q_{max} suddenly increases for $\zeta < \zeta_{\text{ar}} \approx 0.155$ which marks the change from repulsive to attractive interaction at T_{gel} . Below ζ_{ar} q_{max} increases linearly with decreasing ζ . A similar behaviour can be found for S_{max} where ζ_{ar} divides as well two regimes. Note that ζ_{ar} is not a fixed volume fraction such as ζ_0 or ζ_{VFT} but rather divides the measured samples in

an attractive and a repulsive regime which is driven by crossing the LCST. For $\zeta < \zeta_{\text{ar}}$ the
 185 peak height S_{max} is dominated by its temperature dependence, with a minimum at $T = 313$
 K (see Supplementary Material). Above ζ_{ar} the maximum S_{max} follows a master curve for all
 c . In particular, it increases with ζ up to a maximum at ζ_{VFT} and drops slightly for larger ζ .
 The decrease of Δq_{max} in combination with the increasing S_{max} above ζ_{ar} indicates increasing
 order accompanied with a densification, i.e., reduction of next-neighbour distances which is
 190 typical for colloidal liquids approaching crystallisation or vitrification. The maximum at
 ζ_{VFT} has also been reported for other soft colloids at the glass transition volume fraction
 and results from a competition between energy and entropy [12, 28, 30].

Our results indicate glass-liquid and glass-gel transitions in a soft colloidal core-shell
 system. Changing the temperature between 288 K and 318 K, the PNIPAm shell expels
 195 water leading to a decreased particle size and thus change of the effective volume fraction
 ζ . Despite a change of the interaction potential with temperature [15], we observe phase
 changes as function of effective volume fraction independent from temperature.

For weight fractions below 10% the relaxation times obtained by XPCS fall on a master
 curve showing a slowing down following a VFT type. Above $\zeta_0 = 0.51$ the samples fall
 200 out of equilibrium, forming a glass state expressed by a change of the ζ -dependence of τ to
 a less steep, linear slowdown. The VFT volume fraction $\zeta_{\text{VFT}} = 0.84$ and the low kinetic
 fragility index $m^* \approx 1$ match results obtained from pure PNIPAm colloids measured at
 fixed temperature with different number densities [28, 30, 44]. Most importantly, the liquid-
 glass transition shows universal features of soft particles, and only depends on the volume
 205 fraction of the PNIPAm particles. Especially in the liquid state, regions of both attractive
 interaction at small ζ and repulsive states with increasing ζ fall on the VFT master curve.
 Moreover, this VFT behaviour is independent from the particles' softness which changes
 with temperature in our study challenging the role of softness on the glass transition in such
 soft colloids [28, 29, 39, 40].

210 The dynamics of the two highest weight fractions studied follow the linear slowdown
 above ζ_0 . However, different from the samples at $c < 10$ wt.% the relaxation time slows
 down again with decreasing ζ in the regime of attractive interactions. Together with the
 exponents $p \approx 1$ and $\gamma \approx 1.8$ in this regime, the results suggest a glass-gel transition around
 $\zeta_{\text{gg}} = 0.34$. The sample at $c = 10$ wt.% shows an intermediate behaviour, i.e., the dynamics
 215 follows the linear increase of τ above ζ_0 , but matches the VFT curve only for repulsive states.

In the attractive regime, τ is approximately one order of magnitude slower than for the liquid samples. Furthermore, the exponents suggest heterogeneous, subdiffusive dynamics. Interestingly, at 288 K this sample's volume fraction is $\zeta(10\%, 288 \text{ K}) = 1.0$. Below $\zeta = 1$, the particles deform and their effective radius was reported to be stable whereas for $\zeta > 1$ interpenetration is observed [11, 47, 49, 50]. The sample at $c = 10 \text{ wt.}\%$ is at the border between both states. This indicates that once interpenetration of PNIPAm shells is present in the repulsive regime, i.e. $\zeta > 1$, a glass-gel transition takes place, while otherwise the glass-liquid transition occurs.

A particular characteristic is observed at ζ_{gg} . As discussed in the previous paragraph, this volume fraction marks the transition between the glass and the gel state for $c > 10 \text{ wt.}\%$. On the other hand, it coincides with the maximum of p and the minimum of γ , respectively. Such extrema have been reported for soft colloids close to their glass transition [28, 44] and have been related to stress relaxation. In those studies, the sudden increase of γ (and decrease of p) reflected a transition from stretched ($\gamma < 1$) to compressed ($\gamma > 1$) relaxation. This is different in our case, where $\gamma < 1$ is found at both sides of the minimum. Instead, a sudden increase to a compressed exponential takes place between ζ_0 and ζ_{VFT} and reflects the glass transition. Together with the coincidence with the glass-gel transition at larger weight fractions this results suggests a manifestation (or reminder) of the glass-gel transition in the supercooled liquid state. This is rationalized by the interference of glass and gel dynamics that results in anomalous dynamics such as subdiffusion [55] and multiple relaxation processes [56–58]. Both may result in a reduction of γ and increase of p which matches our data.

Compared to the dynamics, the structure factors show a different behaviour. First, $S(q)$ is almost constant at large ζ (see Fig. 2). This suggests a similar structure at high volume fractions due to deformation, deswelling and interpenetration where the dynamics change linearly with ζ . Moreover, relative changes of $S(q)$ follow master curves that reflect the attractive and repulsive regime. In contrast, absolute values of q_{max} and S_{max} are defined by weight fraction c and T , resembling the changing interaction potential due to the swelling of the particles. Interestingly, the dynamics are independent from that change.

The results are summarized in the T - ζ phase diagram shown in Fig. 3. It extends the phase diagram published recently [26]. The reported volume fractions that mark phase borders as well as transitions of structure and dynamics are indicated. In conclusion, our

FIG. 3. T - ζ phase diagram for all samples studied. Colloidal gel regime adapted from [26]. Fluid A refers to the repulsive fluid, fluid B to the attractive fluid state. The glass state is found above ζ_0 .

study on glass-gel and glass-liquid transitions of a thermo-responsive colloidal soft-sphere system provides a detailed view on their structure and dynamics over a wide area of the phase diagram. First, for $c < 10$ wt.% the volume fraction defines the phase, there is only a minor impact from the temperature and thus the interaction potential. Consequently, we found repulsive and attractive liquid phases whose dynamics fall on a joint master curve. Approaching the glass transition, the dynamics follow a VFT law with a kinetic fragility index of approximately 1. Second, if the particle shells are subject to deformation, deswelling as well as interpenetration at low temperatures ($c > 10$ wt.%), a glass-gel transition is found at ζ_{gg} upon heating. Third, we found subdiffusive dynamics in the liquid state with exponents p, γ showing a maximum and minimum at ζ_{gg} suggesting interference of the glass-gel transition as a precursor in the liquid phase. These results motivate new studies in theory and experiments to fully understand the phase behaviour of soft particles at intermediate and high volume fractions.

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