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Anisotropic and heterogeneous dynamics in an aging colloidal gel[†]

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We investigate the out-of-equilibrium dynamics of a colloidal gel obtained by quenching a suspension of soft polymer-coated gold nanoparticles close to and below its gelation point using X-ray Photon Correlation Spectroscopy (XPCS). A faster relaxation process emergent from the localized motions of the nanoparticles reveals a dynamically-arrested network at the nanoscale as a key signature of the gelation process. We find that the slower network dynamics is hyper-diffusive with a compressed exponential form, consistent with stress-driven relaxation processes. Specifically, we use direction-dependent correlation functions to characterize the anisotropy in dynamics. We show that the anisotropy is greater for the gel close to its gelation point than at lower temperatures, and the anisotropy decreases as the gel ages. We quantify the anisotropic dynamical heterogeneities emergent in such a stress-driven dynamical system using higher order intensity correlations, and demonstrate that the aging phenomenon contributes significantly to the properties evaluated by the fluctuations in the intensity correlations. Our results provide important insights into the structural origin of the emergent anisotropic and cooperative heterogeneous dynamics, and we discuss analogies with previous work on other soft disordered systems.

1 Introduction

Tracking the microscopic structure and dynamics in soft disordered materials, such as colloidal gels and glasses, is a subject of long-standing scrutiny and great complexity. The dynamical processes occur over a wide range of length and time scales, slow down with the sample age and can be highly sensitive to the sample history. A large body of experiments using time resolved correlation techniques^{1–13}, confocal microscopy^{14–17}, differential dynamic microscopy¹⁸, and theory and simulations^{19–28} have investigated the dynamics of colloidal gels^{29–31}, providing deep insights into the structural origin of the relaxation mechanism such as caging, localization and cooperative particle rearrangements producing dynamical heterogeneities.

An established model underlying the dynamics and aging observed in colloidal gel systems has been ascribed to the deformation of the elastic network due to local stresses that develop as a gel is formed^{1,19,26,32}. Recent numerical simulations sup-

port this scenario of frozen-in stresses controlling the intermittent microscopic dynamics^{24,27}. However, there is still a limited understanding of how these local restructuring events affect the transmission of stress throughout the contact network where the weakly connected or softer domains may coexist with the stiffer regions. Experiments^{3,16,29} and simulations²⁴ also suggest that these stress-induced local deformations generate large-scale cooperative motions, evidenced by the presence of dynamical heterogeneities, that play a crucial role in evolution of the overall gel dynamics^{3,16,29,33}. However, a direct examination of the consequences of aging on dynamical heterogeneities via experiments and simulations is lacking.

To address these open questions, we use X-ray Photon Correlation Spectroscopy (XPCS) to investigate the dynamics in a colloidal suspension, consisting of polymer coated gold nanoparticles, that transforms from a fluid to the gel state following an onset of a temperature-controlled short-range attraction. We show that the short waiting time dynamics of the colloidal gel is anisotropic and heterogeneous. This behaviour is different than prior observations of colloidal gel dynamics where stress induced deformation is shown to be uniform within the probed volume resulting in isotropic response functions, e.g., decay of the density autocorrelation function or growth of the mean squared displacement of the particles. Here, a range of wave vector transfers and

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time scales accessible with XPCS make it a powerful technique to demonstrate the out-of-equilibrium and anisotropy in gelation dynamics and its corresponding structural origins. We also observe hyperdiffusive dynamics and occurrence of a faster rattling-type particle localization similar to previous experiment demonstrations on other colloidal gel systems^{1–5,8,11,13,32,34}. We show that the initial anisotropy in dynamics vanishes as the gel ages. Finally, we report that the temporal fluctuations in the dynamics are significantly influenced by the sample age and establish a microscopic picture of the evolution of these cooperative processes in accordance with previous simulation and experimental work.

2 Experiment

2.1 Sample preparation and characterization

The suspensions used here consist of gold nanoparticles (AuNP) with a polymer coating of α -methoxypoly(ethylene glycol)- ω -(11-mercaptoundecanoate) (PEGMUA) ligands in a mixed solvent of glycerol and water (70:30 volume/volume). The synthesis of such polymer-coated AuNPs has been described elsewhere^{35–38}. The radius of the gold core is determined to be $r_{core} \simeq 6.15 \pm 0.61$ nm via Transmission Electron Microscopy (TEM). The size dispersity is below 10% as measured previously³⁹. The PEGMUA ligand has a molecular weight of about 5000 g/mol (5kDa), providing a shell thickness in the range of 10–14 nm in pure water as characterized by Dynamic Light Scattering³⁸ (DLS). For our experiment, we use a sample with a total volume fraction of $\sim 6.4\%$, calculated assuming the shell thickness of the nanoparticle in water. For this specific mixing ratio of glycerol-water and colloidal concentration, the suspension transitions into a gel phase as the temperature is decreased below the theta temperature ($T_\theta \geq 280$ K) due to the sudden initiation of a temperature-dependent effective interparticle attraction. The fluid-gel transition is thermoreversible in nature.

2.2 X-ray Photon Correlation Spectroscopy (XPCS) Experiment

The XPCS experiments were performed at the beamline ID10 at the European Synchrotron Radiation Facility (ESRF), Grenoble, France. A small-angle X-ray scattering (SAXS) geometry was used with a partially coherent 8.1 keV x-ray beam of $10 \times 10 \mu\text{m}^2$ size was focused on the sample, and the scattering patterns were recorded with a MAXIPIX 2×2 detector⁴⁰ (pixel size $55 \times 55 \mu\text{m}^2$) located 5.2 m downstream from the sample. The beam size was defined using a compound refractive lens and roller blade slits, and was centered on the corner of the detector to maximize the measurable range of wave vector transfer, q . The fluid samples were filled in 0.7 mm thick borosilicate capillaries (acquired from Hilgenberg GmbH) which were vacuum sealed and placed in an evacuated sample chamber fitted with a Peltier-stage temperature controller. Scattering patterns were corrected for the detector flat field and bad detector pixels. The SAXS data was corrected for the background signals from the capillary and solvents. Sensitivity to radiation damage was carefully checked for and sample-based beam exposure thresholds were determined in preliminary measurements. Previous to measurements at ID10,

Fig. 1 The X-ray scattering intensity, $I(q)$, for the PEGMUA-coated AuNP suspensions at $\phi = 0.064$ in the fluid state at $T_{\text{fluid}} = 298$ K (dashed line) and the gelled state at T^* and $T^* - 2$ K at the shortest waiting time, $t_w^{(0)} = 600$ s. Intensity curves obtained at longer waiting times overlap completely and are not shown here for clarity.

pre-characterization studies were carried out at the beamline P10 of PETRA III, DESY, to determine the gelation temperature, T^* and the relevant q -range using a SAXS experiment set-up similar to the one as described above.

A strict temperature-quenching protocol was followed, where the structural and dynamical evolution of the gel was monitored after quenching the temperature from 298 K to the target temperatures of $T^* = 280$ K and $T^* - 2$ K at a quench rate of ≈ 1.8 K/min. The temperature, T^* , was defined as the temperature where arrested dynamics with a time resolution greater than 1 s was observed upon decreasing the sample temperature from 298 K to 288 K in 5 K steps, subsequently followed by 2 K steps. We note that the value of $T^* = 280$ K is based on the experimental set-up and $T_\theta \geq T^*$. The data was collected at different waiting times, t_w of 600, 1300, 3300 and 5300 s after the target temperature was reached ($t_w = 0$). Each sample filled capillary was heated to 50 °C and kept in an ultra-sonification bath in a timed protocol, in order to erase any memory of the sample's history. Additionally, before reducing the temperature to induce gelation, data was collected at room temperature to ensure the scattering signal was equal to previous measurements from the same sample.

3 Results

3.1 Evolution of microstructure

The SAXS intensity was found to be isotropic around the direct beam position, hence, an azimuthally averaged intensity curve, $I(q)$, is shown in Fig. 1. The intensity of the fluidic suspension at 298 K is slightly elevated at small wave vectors and exhibits a peak at $q \simeq 0.19 \text{ nm}^{-1}$. In contrast, as the suspension forms a gel following the quench, the intensity increases significantly at low q indicating the formation of large-scale structures. In the gelled state, a broad intensity peak is apparent at $q = 0.27 \text{ nm}^{-1}$, implying a denser local packing of the particles due to ligand compression or interpenetration. This structural response of the colloidal suspension at low q and $q > 0.25 \text{ nm}^{-1}$ observed at temperatures, T^* and $T^* - 2$ K, is reminiscent of observations of similar

PEGMUA-coated AuNP colloids in an aqueous solution³⁹ at different pressure conditions, where a smaller ligand shell thickness at higher pressures directly correlates with an increase in effective inter-particle attraction. The intensity profiles in the measured q -range at different waiting times completely overlap, indicating that the averaged microstructure and sample concentration remains unchanged during the measurement.

3.2 Evolution of gel dynamics

3.2.1 Direction-dependent Intensity Correlation functions.

The out-of-equilibrium behaviour generally associated with colloidal gels and other soft disordered solids is captured by the instantaneous two-times correlation function,^{3,11,41–45}

$$C(q, t_1, t_2) = \frac{\langle I(q, t_1) I(q, t_2) \rangle_\phi}{\langle I(q, t_1) \rangle_\phi \langle I(q, t_2) \rangle_\phi} \quad (1)$$

where $I(q, t)$ is the scattered intensity at wave vector transfer q at time t and the averaging $\langle \dots \rangle_\phi$ is done over pixels corresponding to the wave vectors $|q| = q \pm \Delta q$ in an azimuthal angle range of $\phi \pm \Delta\phi$. In particular, we characterize the anisotropy of the evolution of gel dynamics by determining $C(q, t_1, t_2)$ in the vertical ($\parallel$ to the capillary wall) and the horizontal ($\perp$ to the capillary wall) directions. This is done using two sectors of the recorded speckle patterns with an azimuthal angle width of 30° , each defining a triangular region of interest in the vertical and horizontal directions. For a static sample, the two-times correlation, $C(q, t_1, t_2) = 1 + b_0$, where b_0 is the maximum speckle contrast or the Siegert factor determined from the experimental setup. In this geometry, $b_0 = 0.22$ was calculated from measurement of a static polystyrene-based hard sphere sample.

Two examples of normalized two-times correlation, $(C(t_1, t_2) - 1)/b_0$, at $q = 0.07 \text{ nm}^{-1}$ for the gel at $T^* - 2 \text{ K}$ in the vertical and horizontal directions are shown in Figs. 2 (a) and (b), respectively. In this representation, the absolute experimental time is given by $t_{\text{age}} = (t_1 + t_2)/2$ and the delay time is given by $\tau = |t_1 - t_2|$. Thus, the diagonal from the lower left to the upper right corner in the figures corresponds to $\tau = 0$. In both cases, one observes that the contour lines in the correlation function become broader with increasing t_1 (or t_{age}) during the measurement, indicative of aging dynamics in both directions. Additionally, at any value of t_1 , while travelling in the direction perpendicular to the $\tau = 0$ diagonal, the normalized $C(q_{\perp}, t_1, t_2)$ (Fig. 2(b)) decays to 0 at longer delay times than $C(q_{\parallel}, t_1, t_2)$ (Fig. 2(a)) demonstrating slower dynamics in the horizontal direction.

To gain more insight from this 2D representation of the dynamics, we obtain the intensity autocorrelation function, $g_{(2)}$, by averaging the two-times correlation function, $C(q, t_1, t_2)$, at fixed delay times, τ ,

$$g_{(2)}(q, \tau) = \langle C(q, t_1, \tau) \rangle_{t_1} = \left\langle \frac{\langle I(q, t_1) I(q, t_1 + \tau) \rangle_\phi}{\langle I(q, t_1) \rangle_\phi^2} \right\rangle_{t_1}, \quad (2)$$

where the averaging $\langle \dots \rangle_{t_1}$ is performed over a time window which exhibits quasi-equilibrium dynamics, i.e., the contour lines in Figs. 2 (a) and (b) remain parallel to the diagonal. The time

Fig. 2 Normalized two time correlations observed at the shortest waiting time, $t_w^{(0)} = 600 \text{ s}$ at $T^* - 2 \text{ K}$ for $q = 0.07 \text{ nm}^{-1}$ in the (a) vertical and (b) horizontal direction. The white lines at $t_1 = t_2 = 150 \text{ s}$ denote the time window for which the intensity autocorrelation functions, $g_{(2)}$, are calculated; (c) and (d) Normalized intensity autocorrelation functions $(g_{(2)} - 1)/b_0$ vs. delay time, τ , at $T^* - 2 \text{ K}$ for increasing q values obtained by time averaging $\langle C(q, t_1, \tau) \rangle_{t_1}$ for $t_1 = [0, 150] \text{ s}$. The different colors correspond to q values in nm^{-1} of 0.07 (dark blue), 0.085 (blue), 0.115 (cyan), 0.145 (green), 0.175 (yellow), 0.205 (orange), 0.225 (dark red); (e) and (f) Normalized intensity autocorrelation functions for $q = 0.07 \text{ nm}^{-1}$ in the vertical and horizontal directions are shown together for both temperatures at waiting times, $t_w = 600 \text{ s}$ (e) and 5300 s (f).

window for the gel at $T^* - 2 \text{ K}$ was $t_1 = [0, 150] \text{ s}$ as shown by the white lines. The function $g_{(2)}$ is directly related to the decay of the density autocorrelation or the intermediate scattering function, $F(q, \tau)$ as $g_{(2)}(q, \tau) = b_0 |F(q, \tau)|^2 + 1$, where b_0 is the Siegert factor, mentioned earlier. The $g_{(2)}$ curves are typically described using the Kohlrausch-Williams-Watts (KWW) function with a modified stretched exponential form^{46,47}:

$$g_{(2)}(q, \tau) = 1 + b(q) \exp\{-2[\Gamma(q)\tau]^\gamma\}. \quad (3)$$

Here, Γ is the relaxation rate connected to the characteristic relaxation time $\tau_c = 1/\Gamma$, γ is the stretching exponent, and the prefactor b is a measure of the optical contrast and the short-time plateau value of the correlation function.

Figs. 2 (c) and (d) show the normalized intensity autocorrelation functions for the gel at $T^* - 2 \text{ K}$ after $t_w = t_w^{(0)} = 600 \text{ s}$ in the vertical, $q_{\parallel}$ and horizontal, $q_{\perp}$ directions, respectively. We see that the short-time plateau value of the normalized $g_{(2)}$ functions is < 1 , and the functions decay faster in the vertical direction than

in the horizontal direction. The last row in Fig. 2 shows the auto-correlation functions in both directions for the gelled phase comparing the temperatures, T^* and $T^* - 2$ K, for a single q value at the shortest (e) and longest (f) measured waiting times. From this comparison, we clearly see the difference between $g_{(2)}$ functions obtained from the vertical and horizontal directions is greater at T^* than at $T^* - 2$ K at both waiting times. The results of the fits to equation 3 are shown as solid lines in Fig. 2 (c-f), and we discuss the resultant fit parameters in detail below.

In Figs. 3 (a) and (b), the q -dependency of the relaxation rates, Γ , are shown for the shortest and longest measured values of t_w , respectively. The solid lines denote a $\Gamma \propto q$ scaling, which is followed over the whole course of the experiment. This feature has been previously highlighted in several experiments on colloidal gels and other disordered soft matter systems^{1,3-5,8,32,48-50}, theory^{19,26} and simulations²⁷. In these cases, the underlying microscopic dynamics is dominated by the relaxation of randomly distributed stress dipoles within the system and the stretching exponent, γ is close to 1.5. In this work, γ shows a slight temperature dependence with $\gamma(T^*) = 1.3 \pm 0.1$ and $\gamma(T^* - 2 \text{ K}) = 1.4 \pm 0.1$. In Fig. 3 the stretching exponent, γ is fixed at 1.35 to facilitate comparisons of the fit parameters between the dynamics at different temperatures. Recent simulations²⁷ attribute this variation to the ratio of Brownian stresses to the stress heterogeneities developed in the system during gelation where γ is found to be lower when the stress heterogeneities are more dilute at higher temperatures, thus, $\gamma(T^*) < \gamma(T^* - 2 \text{ K})$.

From Fig. 3 (a), at the shortest waiting time $t_w^{(0)}$, the particles are faster in the vertical than in the horizontal direction, i.e., $\Gamma(q_{\parallel}) > \Gamma(q_{\perp})$. In contrast, at the longest waiting time, $t_w = 5300$ s, $\Gamma(q_{\parallel}) \simeq \Gamma(q_{\perp})$ as evident from Fig. 3 (b), suggesting that the network dynamics in the scattering volume is no longer temporally heterogeneous. The observation $\Gamma_{\parallel} > \Gamma_{\perp}$ at the initial waiting times indicates the development of an anisotropic stress field within the sample after it undergoes volume contraction (associated with the gelation transition)^{4,24}. We believe that the anisotropy in the gel dynamics arises due to the different boundary conditions experienced by the newly formed gel in the vertical and horizontal directions within the capillary. One possibility is that an attraction develops between the colloidal particles in the gelled-state and the glass wall causing the gel to adhere to the capillary walls. Thus, the gel is subjected to a free surface in the vertical direction ($\parallel$ to the capillary walls) but a fixed surface in the horizontal direction. This would make the internal stress relaxation within the gel more compliant in the vertical direction than the horizontal direction. We also observe that the asymmetry in the stress relaxation within the scattering volume is the greatest at the earliest waiting times, indicated by the different relaxation rates in the horizontal and vertical directions.

We note that in this experiment, the gravity field is parallel to the capillary wall. However, we rule out the possibility of sedimentation-generated anisotropy as firstly, the $g_{(2)}(q_{\parallel}, t)$ profiles do not exhibit any periodic modulations characteristic of sedimentation flows^{51,52}. Secondly, the relaxation rate does not deviate from the $\Gamma \propto q$ scaling at different waiting times in contrast

Fig. 3 Relaxation rate, Γ vs. $q_{\parallel}$ and $q_{\perp}$ at $t_w = 600$ s (a) and 5300 s (b) for the gel formed at temperatures, T^* and $T^* - 2$ K. Solid lines are fits for $\Gamma \propto q$. Negative logarithm of the non-ergodicity factor b/b_0 vs. $q_{\parallel}^2$ and $q_{\perp}^2$ at $t_w = 600$ s (c) and 5300 s (d) for both temperatures. Solid lines are fits for equation 4. For the KWW-fits (equation 3), the stretching exponent, $\gamma = 1.35$.

to experiments on sedimenting colloids where clear deviations in the Γ - q scaling have been observed between the early and final stages of the experiment⁵². The decrease in the relaxation rates with increasing waiting times in Figs. 3 (a) and (b) also reflects aging dynamics in the gels at both target temperatures. We will discuss this in a later section in detail.

3.2.2 Faster 'unresolved' decay process.

A striking feature of the normalized $g_{(2)}$ functions in Fig 2 (c-d) is that the shorter-delay time plateau value, b/b_0 is less than 1. This 'missing' contrast signals to a faster decay process that could not be resolved in the experiment.[‡] It is well known that in the case of semi-localized fast particle motions, akin to particles rattling in a cage in dense suspensions, the intermediate scattering function $F(q, \tau)$ decays to the so-called non-ergodicity factor, $F(q, \infty)$.^{2-5,7,8,48,53-56} This factor is analogous to the Debye-Waller factor of a solid providing a measure of the degree of struc-

[‡] The Siegert factor, b_0 , displays a complex q -dependence based on the experimental set-up and the beam coherence properties. We estimated a maximum of 5% drop in b_0 at the larger wave vector transfers measured in this experiment, which is negligible compared to the measured drop in contrast.

Fig. 4 (a) The localization length, r_{loc} vs. waiting times, t_w , and (b) fraction of localized particles, f_0 vs. t_w in the horizontal (||) and vertical (⊥) directions at temperatures T^* and $T^* - 2$ K.

tural arrest in the gelled phase:

$$F(q, \infty) = \sqrt{b/b_0} = \sqrt{f_0^2 \exp(-2q^2 \langle r^2 \rangle)} \quad (4)$$

$$\log(b/b_0) = 2\log(f_0) - 2q^2 \langle r^2 \rangle$$

where, the range of the rapid localized motion of the colloids is estimated by $r_{loc} = \sqrt{6\langle r^2 \rangle}$; f_0 denotes the fraction of particles whose dynamics have become localized and $1 - f_0$ is the fraction of non-localized particles in the scattering volume.

In Figs. 3 (c) and (d), the negative logarithm of the ratio b/b_0 vs. q^2 is shown for both target temperatures in the vertical and horizontal directions. A noteworthy feature for the gelled phase at T^* is that the difference in values of b between both directions persists at all measured waiting times, whereas those differences are negligible for the gelled phase at $T^* - 2$ K. The fits to equation 4 are shown as dashed lines, and the corresponding fit parameters, namely, the localization length, r_{loc} and fraction of localized particles, f_0 , associated with the faster ‘unresolved’ decay process, are depicted in Fig. 4. Upon quenching to T^* , $r_{loc,⊥}$ is slightly elevated to $r_{loc,||}$ at all the measured waiting times, while the differences are negligible at $T^* - 2$ K. The decreased value of $r_{loc,||}$ and $r_{loc,⊥}$ for the gelled phase at $T^* - 2$ K in comparison to T^* , suggest a denser and stiffer gel at lower temperatures owing to the higher interparticle attraction strength at lower temperatures. In Fig. 4 (b), $f_{0,||} > 0.95$ and $f_{0,⊥} > 0.95$ at $T^* - 2$ K implying that the fraction of particles with the corresponding localization lengths ($r_{loc,||}$ and $r_{loc,⊥}$) in both vertical and horizontal directions are similar. Furthermore, this fraction of localized particles in both directions varies marginally at the different waiting times. Meanwhile at T^* , $f_{0,||} > 0.95$, however, in the horizontal direction $f_{0,⊥} > 0.65$. This difference in values suggests the existence of a fraction of particles that display localized dynamics in the horizontal direction (while being non-localized in the vertical direction) is $\approx 30\%$ during the entire experiment measurement. This observation of the missing contrast values at T^* combined with the behaviour of the corresponding relaxation times in Fig.3(a) presents an interesting phenomenon at the earliest waiting time, $t_w = 600$ s. It indicates that the gel at T^* has a higher fraction of particles with “fast” lo-

Fig. 5 (a) Relaxation rate, Γ vs. t_w at temperatures, T^* and $T^* - 2$ K during the initial measurement after $t_w^{(0)} = 600$ s at $q_{||} = q_{\perp} = 0.115 \text{ nm}^{-1}$. The solid dashed lines are fits to equation 5. The inset to (a) shows the evolution of Γ vs. t_w at the same q value through the whole experiment. (b) Evolution of q -independent aging velocity, v_{age} during the initial measurement at $t_w^{(0)}$ estimated quantitatively from equation 5.

calized dynamics and simultaneously slower dynamics due to the gel network in the horizontal direction than in the vertical direction. Throughout the duration the measurement, the gel network at T^* becomes stiffer indicated by the decreasing values of r_{loc} . On the other hand, the gel is highly networked at $T^* - 2$ K with a stiffer, isotropic network and a negligible fraction of non-localized particles.

3.2.3 Aging behaviour.

To better understand the aging behaviour of the gel network, we inspect the evolution of the intensity autocorrelation functions with sample age. In this case, we calculate the $g_{(2)}$ functions by performing a running average of the two-times correlation function $C(q, t_1, t_2)$ with a fixed time window using equation 2. We observe that following the gel formation at both target temperatures, the relaxation rate Γ decreases with waiting time t_w in the horizontal and vertical directions at all q values. This dependency is depicted close to the shortest waiting times in Fig. 5(a) at $q = 0.115 \text{ nm}^{-1}$. The physical picture underlying this behaviour has been previously interpreted for colloidal gels, where the internal stress produces a series of microcollapses or local reorganization events leading to a stiffening of the elastic network, i.e., a lower energy state, which in turn causes the newly developed stress sources to decay with a longer lifetime.^{19,29,32} The relationship between Γ and t_w arises from the complex interdependence of the number of active stress sources within the area and their lifetime.³² The relaxation rate for all waiting times is shown in the inset to Fig. 5(a), where the differences between the relaxation rates in both directions vanish for $t_w > 1300$ s at T^* and for $t_w > 600$ s at $T^* - 2$ K. From the inset, it is evident that Γ does not decay inversely proportional to t_w at longer waiting times, but due to sparseness of the recorded data, we focus on the earlier aging regime at $t_w^{(0)} = 600$ s.

For both temperatures, along the vertical and horizontal directions, the t_w dependency of Γ can be empirically described by a

Table 1 Values of the aging parameters, α and τ_0 from equation 5 for the gel at different conditions.

T	direction	α (1/nm)	τ_0 (s)
$T^* - 2$ K	$\parallel$	0.031 ± 0.001	-390 ± 14
$T^* - 2$ K	$\perp$	0.052 ± 0.002	-316 ± 18
T^*	$\parallel$	0.025 ± 0.001	-484 ± 7
T^*	$\perp$	0.033 ± 0.001	-430 ± 20

linear equation,

$$\Gamma(q, t_w) = \frac{q}{\alpha(t_w + \tau_0)} \quad (5)$$

where in this case, α and τ_0 are parameters based on the direction and temperature⁵⁷. Here, the relationship $\Gamma \propto (t_w + \tau_0)^{-1}$, presents a deviation from the simple aging behaviour observed in several soft glassy systems^{7,20,29,30,58}, where $\tau_0 = 0$. The negative values of τ_0 suggest that the aging dynamics may have commenced (or, the target temperature was reached) a few minutes earlier than the exact time indicated by the sample chamber temperature controller.

One can further approximate^{5,32,57}, $\Gamma = q\langle v_{\text{age}} \rangle$, and quantitatively estimate a q -independent stress induced aging velocity, $\langle v_{\text{age}} \rangle$ as follows: $\langle v_{\text{age}} \rangle = (\alpha(t_w + \tau_0))^{-1}$. The solid dashed lines displayed in Fig. 5(a) are fits to equation 5 at $q = 0.115 \text{ nm}^{-1}$, and the corresponding aging velocities in both horizontal and vertical directions are shown in Fig. 5(b). The values of the parameters, α and τ_0 are given in Table 1. To avoid radiation damage, the total exposure time for the sample at T^* was less than at $T^* - 2$ K resulting in fewer measurements (with larger error bars) at T^* from which the aging velocity parameter could be extracted.

It is evident from Fig. 5(b) that the gel ages faster at T^* than at $T^* - 2$ K. The gel also ages faster in the horizontal than in the vertical direction at both temperatures. This follows from the “micro-collapse” aging model described above, where the restructuring events are more likely to occur in regions where the gel network is weaker and particles are relatively more mobile, thus, directly influencing the sample’s aging rate. The local environment of the gel becomes stiffer with time, reducing the softness, making subsequent rearrangements harder and the aging rate slowly decays, as observed here.

3.2.4 Dynamical heterogeneities.

The instantaneous two-times correlation functions combined with the anisotropic dynamics and aging behaviour shown in above figures strongly indicate features revealing dynamic heterogeneity. A useful quantity to describe dynamic heterogeneities is the temporal fluctuations of $C(q, t_1, t_2)$ given by its normalized variance^{3,6,11,42–44},

$$\chi_t(q, \tau, t_{\text{max}}) = \frac{\langle C^2(q, t_1, t_1 + \tau) \rangle - \langle C(q, t_1, t_1 + \tau) \rangle^2}{b^2(q)}. \quad (6)$$

Here, the $\langle \dots \rangle = \frac{\sum_{t_1=0}^{t_{\text{max}}-\tau} \dots}{t_{\text{max}} - \tau}$. The quantity t_{max} directly relates to the sample age, i.e. after the first measurement at $t_w^{(0)}$, $t_{\text{max}} = t_w - t_w^{(0)}$. In order to compare χ_t at different q values, we use a normalization factor, $b^2(q)$, representing the square of the short-time plateau value (or optical contrast) of the correspond-

ing intensity autocorrelation functions³ (shown in Figs.2(c-f) and the same quantity described in equation 3).[§] For the measurement at $T^* - 2$ K, t_{max} ranges from 0 to 250 s (as also shown in Figs. 2(a) and (b)).

χ_t is similar to the dynamical four-point susceptibility, $\chi^{(4)}$, that measures the dynamical *spatial* heterogeneity and has been widely used to study a range of disordered materials approaching the glass or jamming transition^{59,60}. A higher value of $\chi^{(4)}$ is indicative of an increasing length scale over which the particle dynamics is cooperative, suggesting fewer dynamically independent regions in the scattering volume and thus, an increase in the temporal fluctuations experimentally measured by χ_t . It is important to note that χ_t evidences the presence of dynamical heterogeneities under the assumption that the overall system dynamics is stationary and in equilibrium. For non-equilibrium systems, such as the colloidal gel investigated in this work, the quantity χ_t also includes contributions that arise due to the slowing of the dynamics due to aging as the average value of $C(q, t_1, t_2)$ at a given delay time, τ , does not remain constant. We model this “aging” contribution to the normalized variance, χ_t , as $\sigma_{g(2), \tau}^2$ at $t_w^{(0)}$ using a procedure described previously⁴². Details of the model are given in the ESI†, where all parameters in the model are previously known by the experiment. We also subtract the contribution of statistical noise from χ_t ^{33,42}.

In Fig. 6, we track the direction-dependent dynamical heterogeneity and the corresponding aging contribution vs. delay times, τ , at $q = 0.07 \text{ nm}^{-1}$ with the sample age, $t_w^{(0)} + t_{\text{max}}$, where $t_w^{(0)}$ is the shortest waiting time at $T^* - 2$ K. The χ_t curves in both directions depict a well-defined peak for values of $t_{\text{max}} \geq 190$ s, however, we also observe that in the vertical direction (Fig. 6(a)), the emergent fluctuations can be perfectly explained by the aging phenomenon for values of t_{max} upto 250 s. At the highest value of t_{max} , the calculated χ_t curve is slightly elevated than the corresponding aging contribution, suggesting the existence of dynamical heterogeneities in the vertical direction. Interestingly, the peak amplitude of the χ_t curve increases with sample age (t_{max}) and is a direct outcome of the aging behaviour of the colloidal gel in the vertical direction. Unfortunately, to prevent radiation damage, the data could not be collected for times longer than 250 s. On the other hand in the horizontal direction (Fig. 6(b)), that displays slower dynamics and slower aging than the vertical direction, the contribution due to aging is significantly reduced in comparison to the measured temporal fluctuations, χ_t . Thus, in the horizontal direction, χ_t clearly signals the presence of heterogeneous cooperative dynamics. In this direction, the peak amplitude of the dynamical heterogeneity curves, an indicator of the length-scale associated with the heterogeneous cooperative dynamics^{61,62}, maintains a similar value with increasing sample age.

The importance of understanding the influence of aging in the analysis of the fluctuations of $C(q, t_1, t_2)$ has been previously reported for colloidal systems⁴² and non-equilibrium structural

[§] We note that b is simply the variance of the intensity fluctuations divided by the square of the mean intensity

Fig. 6 (a) χ_t at $q_{\parallel} = 0.07 \text{ nm}^{-1}$, and (b) χ_t at $q_{\perp} = 0.07 \text{ nm}^{-1}$ for different values of $t_{\max}$ at $t_w = 600 \text{ s}$ for the gelled phase at $T^* - 2 \text{ K}$. The black lines denote the corresponding aging contribution, $\sigma^2_{g(2), \tau_c}$. The curves have been offset for clarity with a value of 4 in (a) and 8 in (b).

glasses⁵⁷. However, to the best of our knowledge, this is one of the first instance where the contribution due to the anisotropic aging behaviour is explicitly addressed in the evaluation of dynamical heterogeneities measured by the temporal fluctuations of $C(q, t_1, t_2)$ in a colloidal gel. We demonstrate from our analysis that the temporal fluctuations in the vertical direction are dictated by the aging behaviour, whereas in the horizontal direction, the temporal fluctuations are not governed by the aging behaviour and evidence the presence of dynamically heterogeneities. We also observe similar behaviour for higher value of q 's upto 0.12 nm^{-1} (not shown here).

We track the q dependency of τ^* (the delay time corresponding to the maximum value of χ_t) for the gel at both temperatures, and discover that $1/\tau^* \propto q$ similar to the q -scaling of the characteristic relaxation rate (in both directions). We report this result in the ESI, along with χ_t curves for different waiting times, t_w , at $q = 0.07 \text{ nm}^{-1}$.

4 Conclusions

Here, we report the temporal evolution of the microscopic structure and dynamics of gelation of a colloidal suspension, consisting of soft polymer shell-coated colloids, following the introduction of a sudden temperature-induced attractive interaction. The key observations of the system dynamics measured by the intensity autocorrelation functions, $g_{(2)}$: (i) a faster rattling motion of localized particles indicated by a suppression of the short-time $g_{(2)}$ value, (ii) a compressed exponential shape of $g_{(2)}$ ($\gamma \sim 1.35$) and

$\Gamma \propto q$ scaling, support the existing explanation of a two-step relaxation process, where the slower gel network dynamics is governed by stress-driven dynamics^{1,4,32}.

Using direction-dependent intensity autocorrelation functions and temporal fluctuations of the two-times intensity correlation functions, we further arrive at a complex microscopic picture of the gel dynamics and aging. Our results can be summarized as follows: Upon quenching to temperatures equal to or lower than T^* , the intensity correlation functions reveal a sudden onset of dynamic arrest within the scattering volume where particles also become localized. Due to shrinkage during gelation, a non-uniform stress field (or distribution of stress dipoles) develops within the region leading to anisotropic dynamics, where particles in the vertical direction are relatively more mobile than those in the horizontal direction. As the gel ages, the distribution of the stress points homogenizes and the relaxation rates in both directions equalize. The gel formed at T^* exhibits faster dynamics than the gel formed at $T^* - 2 \text{ K}$. Interestingly, the correlation functions indicate that in the gelled phase at T^* , a small fraction of particles in the horizontal direction always remain non-localized during the entire experiment time.

At shorter waiting times near $t_w^{(0)}$, the gel exhibits an aging regime where the relaxation rate decreases linearly with t_w , and grows proportional to q . The gel formed at T^* contains more weaker regions and undergoes a faster aging behaviour than the gel at $T^* - 2 \text{ K}$, which is consistent with previous arguments on gel restructuring investigated in experiments⁶³ and simulations^{24,25}. The local stress-induced microcollapses directly couple with the larger-scaled cooperative rearrangements^{24,25,64}, indicated by the existence of dynamical heterogeneities at low q 's in the range of $0.07 - 0.12 \text{ nm}^{-1}$, however, we distinctly capture the dynamical heterogeneities in the “slower” horizontal direction. In the vertical direction, the temporal fluctuations of the two-times correlation is governed by the aging process. The heterogeneity decays at a rate proportional to q similar to the q -dependency of the characteristic relaxation rate of the system. Most importantly, our XPCS experiment reveals the emergent stress-driven non-equilibrium dynamical processes— particle localization, slower network dynamics, large-scale cooperative motion, aging – in a colloidal gel, highlighting its intricate dependence on direction and the probed length- and time-scales.

To further explore the effects of aging and temperature on the cooperative dynamics and the emergent anisotropic dynamics in these systems, future experiments should study the dynamics for durations longer than reported in this work. Furthermore, with the advent of next generation storage rings^{65,66} and faster detectors^{67,68}, one can examine the faster transient localization process⁹ that is dominated by the Brownian motion of the particles rather than the stress relaxation of the gel network, and provide a more holistic view of the dynamics of a colloidal gel. Investigating the exact conditions which create spatial and temporal heterogeneity in the gel would greatly deepen our understanding of the delicate process of gelation, i.e., the coupling of various dynamical processes over a broad range of length- and time-scales, and have important implications for designing and reverse engineering materials with target mechanical and rheological behaviour.

Conflicts of interest

There are no conflicts to declare.

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