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Length scale dependence of dynamical heterogeneity in a colloidal fractal gel

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We use time-resolved dynamic light scattering to investigate the slow dynamics of a colloidal gel. The final relaxation of the intensity autocorrelation function is faster than exponential: $g_2(q, \tau) - 1 \sim \exp[-(\tau/\tau_f)^p]$, with $\tau_f \sim q^{-1}$ and p decreasing from 1.5 to 1 with increasing q . We quantify dynamical fluctuations by means of the variance $\chi(\tau, q)$ of the instantaneous autocorrelation function, the analogous of the dynamical susceptibility χ_4 studied in glass formers. The amplitude of χ is found to grow linearly with q . We propose a simple model based on intermittent rearrangements that accounts for both the average dynamics and its fluctuations.

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Soft matter systems where the constituents are packed at high volume fraction or interact strongly have a dynamical behavior reminiscent of that of molecular glasses [1]: they exhibit very slow relaxations, non-exponential response or correlation functions, history-dependent dynamics, and dynamical heterogeneity [2]. However, soft glassy systems may also exhibit peculiar dynamical features not found in hard glasses, because of the wider variety of structures and interactions. An example is provided by low volume fraction colloidal gels resulting from the aggregation of strongly attractive particles. In these gels, the decay of the intensity correlation function $g_2(q, \tau) - 1$ measured by dynamic light scattering is steeper than exponential and the relaxation time, τ_f , has an anomalous q^{-1} dependence on the scattering vector [3]. This “compressed” exponential, ballistic-like dynamics has to be contrasted with the stretched exponential relaxations and the diffusive behavior ($\tau_f \sim q^{-2}$) usually found in molecular systems [1]. Quite intriguingly, this unusual dynamics is not restricted to colloidal gels, but has been observed recently in a large variety of soft systems including closely packed deformable spheres, micellar polycrystals, sponge phases, and suspensions of charged particles [4, 5, 6, 7, 8].

These systems share some common features: they all are out-of-equilibrium and thus slowly evolve towards a more stable configuration (aging); moreover, the relaxation of internal stress is believed to play a crucial role in their dynamics [2]. Indeed, for colloidal gels it has been proposed that the dynamics be due to the evolution of strain fields set by dipolar sources of internal stress [3, 5, 9]. At a microscopic level, stress is presumably accumulated by local rearrangements, such as the formation of new bonds and/or bond breaking (“microcollapses” in the language of ref. [9]). These rearrangements are the elementary steps in the direction of a more stable, compact structure. This picture implies that the slow dynamics should not be continuous but rather temporally heterogeneous. Experiments on similar gels, albeit at higher concentration ($\varphi \sim 0.1$ as opposed to $10^{-3} - 10^{-4}$) and in the multiple scattering regime [10],

have indeed suggested qualitatively that the dynamics is intermittent. However, no q -resolved information was provided by these experiments, a crucial missing in the attempt to build a unified understanding of both the average dynamics and its temporal fluctuations, especially in view of the peculiar q dependence of $g_2(q, \tau) - 1$.

In this Letter, we investigate the dynamics of strongly attractive colloidal gels at q vectors spanning one decade, using time-resolved dynamic light scattering. We find that at all q the final relaxation of the average intensity correlation function $g_2(q, \tau) - 1$ is well fitted by a compressed exponential with the same q^{-1} dependence of τ_f as observed previously [3], and with $p > 1$. While at the lowest q $p \approx 1.5$ (as in ref. [3]), at larger scattering vectors p decreases approaching one. We show that the dynamics is temporally heterogeneous and quantify the fluctuations of the dynamics by means of a “multi-point” correlation function χ analogous to the dynamical susceptibility χ_4 introduced in simulations of glass formers [11, 12, 13]. We find that χ increases linearly with q and introduce a simple model of intermittent dynamics that accounts for both the average dynamics and its temporal fluctuations.

The gels are made of polystyrene particles of radius 10 nm suspended in a buoyancy matching mixture of H₂O and D₂O (45/55 by volume). The particle suspension is mixed with a MgCl₂ solution in order to induce particle aggregation in the DLCA regime [14]. The final particle volume fraction and salt concentration are $\varphi = 6 \times 10^{-4}$ and 10 mM, respectively. A gelled structure is obtained after about 2 hours. This space-filling network is formed by interconnected fractal clusters of radius $R_c \approx 10 \mu\text{m}$, as revealed by a peak in the static scattered intensity at $q_{\text{max}} \approx 0.1 \mu\text{m}^{-1}$ [3, 14]. The dynamics of the gel slows down with age [3]: here, we focus on a time window $280\,000 \text{ sec} < t_w < 300\,000 \text{ sec}$, where $t_w = 0$ is the time when the gel is formed. This time window is short enough to prevent significant aging during the experiment.

The gel dynamics is measured by using a charge-coupled device (CCD) camera-based light scattering apparatus similar to that described in [15], slightly mod-

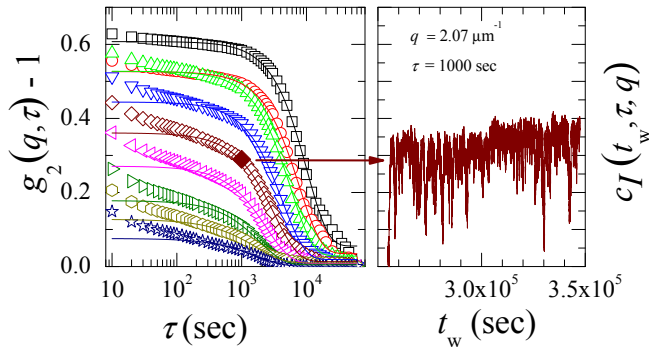


FIG. 1: (Color online) Left panel: $g_2(q, \tau) - 1$ for a gel at $\varphi = 6 \times 10^{-4}$, measured simultaneously at various q vectors. From left to right, q varies from 0.74 to $5.22 \mu\text{m}^{-1}$. The lines are compressed exponential fits to the final relaxation of $g_2 - 1$. Right panel: instantaneous degree of correlation $c_I(t_w, \tau, q)$ for $\tau = 1000$ sec and $q = 2.07 \mu\text{m}^{-1}$; the strong fluctuations demonstrate that the dynamics is temporally heterogeneous. The time average of the signal shown in the right panel corresponds to the solid diamond in the left panel.

ified to access larger q vectors. The setup allows us to measure the dynamics simultaneously at several q 's ($0.4 \mu\text{m}^{-1} \leq q \leq 5.5 \mu\text{m}^{-1}$), corresponding to length scales intermediate between the particle size and the cluster size. In order to access both the average dynamics and its temporal fluctuations, we use the time-resolved correlation (TRC) scheme [10, 16]. The degree of correlation between pairs of images of the light scattered at time t_w and $t_w + \tau$ is calculated according to $c_I(t_w, \tau, q) = G_2(t_w, \tau) / \left(\langle I_p(t_w) \rangle_p \langle I_p(t_w + \tau) \rangle_p \right) - 1$, where $G_2(t_w, \tau) = \langle I_p(t_w) I_p(t_w + \tau) \rangle_p$ and $I_p(t)$ is the scattered intensity at pixel p and time t . $\langle \dots \rangle_p$ is an average over a ring of pixels corresponding to the same magnitude of \mathbf{q} but different azimuthal orientations. The usual intensity autocorrelation function is $g_2(q, \tau) - 1 = \overline{c_I(t_w, \tau, q)}$, where $\overline{\dots}$ indicates a time average. Dynamical fluctuations are quantified by the temporal variance of c_I at fixed τ and q [10, 16].

The average dynamics is shown in the left panel of fig. 1 for several q 's. At all scattering vectors, $g_2(q, \tau) - 1$ exhibits an initial decay, followed by a slightly tilted plateau and a final relaxation. The initial decay is barely observable due to the limited frame rate of the CCD camera; it is due to overdamped, thermally activated fluctuations of the gel strands [17]. The height a of the plateau is related to the average amplitude, δ_p , of these fluctuations by $a \sim \exp(-q^2 \delta_p^2 / 3)$ [17], where $\delta_p = 490 \pm 150$ nm for our gel. The final relaxation is well fitted by a compressed exponential decay: $g_2(q, \tau) - 1 = a \exp[-(\tau/\tau_f)^p]$, where a , τ_f , and p depend on q .

Figure 2 shows the q dependence of p for the experiments reported here (solid circles) and those, on a similar gel, of ref. [3] (semiopen circles). Collectively, the data indicate that the stretching exponent saturates at $p \approx 1.5$

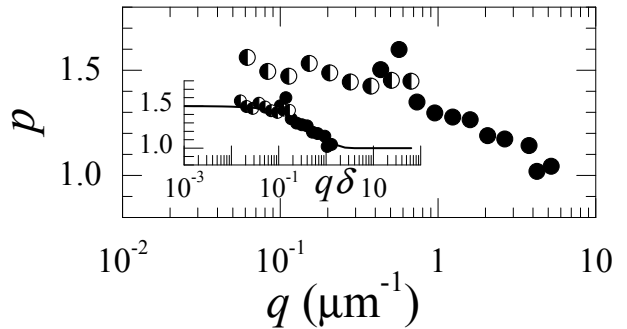


FIG. 2: Exponent p obtained by fitting the final decay of $g_2(q, \tau) - 1$ to a compressed exponential. Filled circles: this work; semiopen circles: ref. [3]. Inset: same data and results of the model described later in the text (line), as a function of the dimensionless scattering vector $q\delta$, with $\delta = 250$ nm.

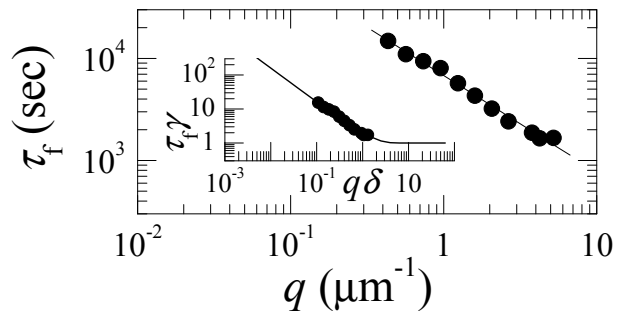


FIG. 3: Symbols: relaxation time τ_f obtained by fitting the final decay of $g_2(q, \tau) - 1$ to a stretched exponential. The line is a power law fit yielding an exponent -0.94 ± 0.03 . Inset: same data and results of the model (see text) vs $q\delta$, with $\delta = 250$ nm and $\gamma = 10^{-3}$ Hz.

at very small q and decreases towards $p = 1$ at larger scattering vectors. Note that a similar decreasing trend of p with q has also been reported for other systems where $p > 1$ [6, 8], although its origin remained unclear. The q dependence of the relaxation time is shown in Fig. 3. We find $\tau_f \sim q^{-0.94 \pm 0.03}$, consistently with measurements at lower q [3]. This behavior rules out diffusive motion, for which $\tau_f \sim q^{-2}$; it rather indicates that the particle displacement increases linearly with time.

The right panel of Fig. 1 shows the time evolution of a representative degree of correlation. The large fluctuations of $c_I(t_w, \tau, q)$ demonstrate unambiguously that the dynamics is temporally heterogeneous. In order to quantify the fluctuations of the dynamics, we calculate $\chi(\tau, q)$, the variance of c_I corrected for the measurement noise contribution [16]. As discussed in refs. [16, 18], this quantity is the analogous in light scattering experiments of the dynamical susceptibility χ_4 much studied in theoretical and numerical works on glass formers [11, 12, 13] and recently investigated in simulations of gels [19]. In order to compare data taken at different q vectors, we focus on the relative fluctuations by normalizing the variance of c_I

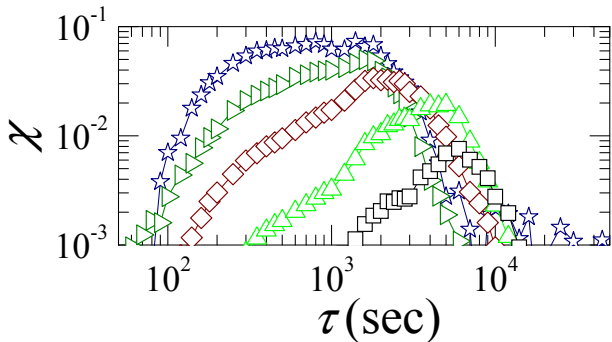


FIG. 4: Dynamical susceptibility $\chi(\tau, q)$ for several q vectors (same symbols as in Fig. 1). From left to right, $q = 0.74, 1.24, 2.07, 3.78,$ and $5.22 \mu\text{m}^{-1}$. To avoid overcrowding the plot, not all the curves at the available q 's have been displayed.

with respect to the amplitude of the final decay of $g_2 - 1$: $\chi(\tau, q) = a^{-2} \left[\overline{c_I(t_w, \tau, q)^2} - (g_2(q, \tau) - 1)^2 \right]$. Results for some representative q vectors are shown in Fig. 4: for all q , χ has a peaked shape, the peak position corresponding approximately to the decay time of the average correlation function, as observed in previous simulations and experiments [12, 16, 18, 19, 20]. Surprisingly, the height of the peak, χ^* , increases strongly with q , in contrast with recent measurements in a granular system where the peak of χ_4 showed virtually no q dependence [20]. For the gels, $\chi^* \sim q^{1.13 \pm 0.11}$, as shown in Fig. 5. To understand this nearly linear growth, we propose a simple scaling argument. As suggested by the highly intermittent behavior of c_I , we assume the slow dynamics to be due to a series of discrete rearrangement events, which we take –for simplicity– to have equal amplitude. Within this scenario, the fluctuations of c_I are due to fluctuations of the number $n(t_w, \tau)$ of events occurring between t_w and $t_w + \tau$; thus $\chi \sim \overline{(n - \bar{n})^2} / \bar{n}^2 = \bar{n}^{-1}$, where the last equality derives from the Central Limit theorem. Because the average number of events scales with the observation time τ , for $\tau = \tau_f$ one obtains $\chi^* \sim \chi(\tau_f) \sim \overline{n(\tau_f)}^{-1} \sim \tau_f^{-1} \sim q$, in very good agreement with the data.

In order to capture not only the scaling of χ^* vs q but also its absolute magnitude and the q dependence of the final relaxation of g_2 , we further develop our simple model of intermittent dynamics. We write $c_I(t_w, \tau, q) = h[n(t_w, \tau), q]$ and

$$g_2(\tau, q) - 1 = \sum_{n=0}^{\infty} P_\tau(n) h(n, q) \quad (1)$$

$$\chi(\tau, q) = \sum_{n=0}^{\infty} P_\tau(n) [h(n, q) - (g_2(\tau, q) - 1)]^2. \quad (2)$$

Here $h(n, q)$ is the correlation left when n events have occurred and $P_\tau(n)$ is the probability of actually observing

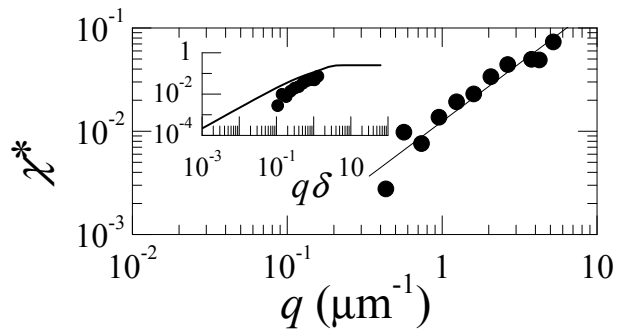


FIG. 5: Peak of the dynamical susceptibility as a function of q (solid circles). The line is a power law fit with an exponent 1.13 ± 0.11 . Inset: same data and results of the model (see text), as a function of $q\delta$, with $\delta = 250$ nm.

n events during a time span τ . In writing Eq. (2), we have assumed that the dynamics is spatially correlated over a length scale much larger than the size of the scattering volume, so that fluctuations are not reduced by averaging the collected signal over several dynamically independent regions [12, 13]. Direct measurements of the spatial correlation of the gel dynamics support this hypothesis [23]. Therefore, in the case of the gel χ is dictated only by the *temporal* heterogeneity of the dynamics. This has to be contrasted with experiments on granular materials [20] and hard spheres [21] and numerical and analytical works on glass formers [11, 12, 13], where χ_4 reflects also the *spatial* correlation of the dynamics.

In order to calculate g_2 and χ from Eqs. (1,2), we need expressions for P_τ and h . For the former, we choose for simplicity a Poisson distribution: $P_\tau(n) = \exp(-\gamma\tau)(\gamma\tau)^n/n!$, corresponding to random rearrangement events affecting the scattering volume at an average rate γ . For the latter, we write $h(n, q)$ in terms of the displacement field generated by n rearrangement events. The q^{-1} scaling of the relaxation time suggests a drift mechanism where the displacement increases linearly with time and thus with the number of events. Therefore, the typical displacement after n events is n times that due to one single event. The correlation left after n events is then $h(n, q) = \langle \exp(-in\mathbf{q} \cdot \Delta\mathbf{R}) \rangle$ [22], where $\Delta\mathbf{R}$ is the particle displacement due to one single event and the average is taken over all possible orientations of \mathbf{q} and over all particles. By assuming that the displacement field is due to the strain of the gel under the action of dipolar sources of internal stress [5, 9] and following ref. [5] one has $h(n, q) = \exp[-(qn\delta)^\beta]$, where δ is the typical displacement of the particles due to one single event and β is equal to 1.5.

We insert the above expressions for P_τ and h in Eqs. (1,2) and calculate both the average dynamics and its fluctuations. The resulting $g_2(\tau, q) - 1$ is very well approximated by a compressed exponential decay, in agreement with the experimental data. We show in the in-

set of Fig. 2 the compressing exponent p issued from the fit of the model, as a function of the dimensionless scattering vector $q\delta$ (line). For $q\delta \rightarrow 0$, we find $p \rightarrow \beta = 1.5$. At larger scattering vectors, p decreases approaching one. Indeed, when the typical displacement is much larger than the length scale $1/q$ probed by light scattering ($q\delta \gg 1$) one single event is sufficient to lead to a complete decorrelation of the scattered light and $h(n, q) \approx 0$ for $n > 0$. The only non vanishing term in the r.h.s. of Eq. (1) corresponds then to $n = 0$, yielding $g_2(q, \tau) - 1 = \exp(-\gamma\tau)$ independently of q . The inset shows also the experimentally determined p . A very good agreement between the model and the experiments is found by setting $\delta = 250$ nm. Remarkably, this value is of the same order of magnitude of the amplitude of the fluctuations of the gel strands due to thermal motion ($\delta_p = 490$ nm). This strongly supports the intuitive picture that the rearrangement events correspond to the formation of new bonds and/or the breaking of the bonds along the gel network. Since both processes are ultimately triggered by thermal energy, they would typically cause particle displacements comparable to those due to the thermal fluctuations of the gel. The average ballistic dynamics would thus be the result of a slow compaction of the gel that proceeds by discrete rearrangements rather than continuously. The relaxation time extracted from the fit of the model is shown as a line in the inset of Fig. 3. For $q\delta < 1$, $\tau_f \sim q^{-1}$, a consequence of the assumption that the typical displacement scales linearly with n . At larger $q\delta$, τ_f saturates to γ^{-1} since in this regime g_2 relaxes exponentially with a characteristic time dictated only by the rearrangement rate γ . By using the same value $\delta = 250$ nm as determined above, we find that the experimentally measured τ_f falls onto the theoretical curve when choosing $\gamma = 10^{-3}$ Hz, corresponding to an average time between events of 1000 sec.

Having fixed the three parameters β , δ , and γ , we now compare the theoretical predictions for the dynamical susceptibility to the experiments. We find that χ has the same peaked shape as for the experiments; the height of the peak is shown in the inset of Fig. 5 (line) together with the experimental points (filled circles). The model captures correctly the linear growth of χ^* with q and the order of magnitude of the dynamical fluctuations, although it overestimates them by about a factor of two. Given the simplicity of the assumptions and the fact that no adjustable parameter has been introduced specifically for χ , this agreement is quite remarkable, showing that the model captures the essential physics of the slow dynamics of the gel. Interestingly, the $\chi^* \sim q$ growth at low q and the saturation regime at large q are similar to asymptotic predictions for $\chi_4(\tau, q)$ in glass formers proposed very recently by Chandler et al. Indeed, in ref. [24] a saturation regime at large q and a $\chi_4 \sim q^2$ scaling for $q \rightarrow 0$ are identified, the q^2 rather than q dependence being the consequence of diffusive rather than ballistic-like

dynamics.

As a concluding remark, we note that although some of the ingredients of our model and their physical interpretation are specific to the colloidal gels, the underlying picture of intermittent rearrangements driven by internal stress may apply also to other soft systems whose average dynamics shares the same features of the gels [4, 5, 6, 7, 8]. Indeed, we find similar results for 2D foams, where the dynamics is driven by the relaxation of internal stress due to coarsening. More time-resolved experiments will be needed to fully test the generality of these ideas.

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