Universal non-diffusive slow dynamics in aging soft matter

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We use conventional and multispeckle dynamic light scattering to investigate the dynamics of a wide variety of jammed soft materials, including colloidal gels, concentrated emulsions, and concentrated surfactant phases. For all systems, the dynamic structure factor $f(q,t)$ exhibits a two-step decay. The initial decay is due to the thermally activated diffusive motion of the scatterers, as indicated by the q^{-2} dependence of the characteristic relaxation time, where q is the scattering vector. However, due to the constrained motion of the scatterers in jammed systems, the dynamics are arrested and the initial decay terminates in a plateau. Surprisingly, we find that a final, ultraslow decay leads to the complete relaxation of $f(q,t)$, indicative of rearrangements on length scales as large as several microns or tens of microns. Remarkably, for all systems the same very peculiar form is found for the final relaxation of the dynamic structure factor: $f(q,t) \sim \exp[-(t/\tau_s)^p]$, with $p \approx 1.5$ and $\tau_s \sim q^{-1}$, thus suggesting the generality of this behavior. Additionally, for all samples the final relaxation slows down with age, although the aging behavior is found to be sample dependent. We propose that the unusual ultraslow dynamics are due to the relaxation of internal stresses, built into the sample at the jamming transition, and present simple scaling arguments that support this hypothesis.

I   Introduction

Disordered, solid-like materials are ubiquitous in soft condensed matter. They range from foams to polymer or particle gels, concentrated emulsions or colloidal suspensions. These materials, whose applications are countless, are typically obtained by a fluid-to-solid transition, which often quenches the system in a far-from-equilibrium configuration. Recent work has focused on the shared features of the solid–fluid transition in disordered materials, leading to the introduction of the concept of *jamming*. Liu and Nagel[1] have proposed a 3-dimensional jamming transition phase diagram, which unifies a wide range of fluid–solid transitions; Trappe *et al.*[2] have shown that a jamming phase diagram can indeed be established for a large variety of attractive colloidal systems. Other recent investigations have also pointed out the similarities between jammed systems such as gels and glasses.[3,4] In jammed systems, the mobility of the constituents is extremely reduced, due to

their crowding, and/or to the presence of strong attractive or repulsive interactions. Conversely, a jammed system may be fluidized by applying an external stress σ that exceeds a critical yield stress.

Despite the advances in the rationalization of the jamming transition, the behavior of soft materials in the jammed phase itself is still poorly understood. One of the most striking features of jammed, out-of-equilibrium colloidal systems, as well of other glassy materials,[5,6] is their aging behavior: sample properties as measured by correlation or response functions change continuously with time, as the sample evolves very slowly towards equilibrium. In particular, these systems exhibit ultraslow relaxations, whose characteristic time increases with age. Dynamic light scattering (DLS) provides a unique tool to probe the slow dynamics and the aging without perturbing the system; moreover, the introduction of new techniques, such as the multispeckle method,[7,8] overcomes the difficulties traditionally posed by ultraslow, non-stationary dynamics and non-ergodicity.[9]

In this paper, we present light scattering measurements of the ultraslow dynamics and the aging of several soft matter jammed systems. Remarkably, we find that for all systems the dynamic structure factor exhibit the same very unusual behavior: at long times an ultraslow, "compressed-exponential" relaxation, whose characteristic time scales as the inverse scattering vector, leads to the complete loss of correlation of the scattered light. This behavior is in sharp contrast with the diffusive or sub-diffusive, slower-than-exponential relaxation typically observed when approaching the jammed phase from the fluid side. We propose a simple model to explain these uncommon dynamics, based on the relaxation of internal stresses, which are built in the sample at the jamming transition. The observation of the very same dynamics in systems ranging from tenuous colloidal fractal gels to concentrated emulsions, and from lamellar gels to micellar polycrystals suggests the generality of this behavior in disordered, jammed, soft materials, underlying the central role of stress relaxation on the system evolution.

The paper is organized as follows: in Section II we present the four experimental systems investigated and we recall the main features of the multispeckle light scattering technique, while in Section III we show the experimental results and briefly discuss the fast dynamics. The ultraslow dynamics, which represents the main focus of the paper, is discussed in Section IV.

II Materials and methods

The colloidal gels are obtained by salt-induced aggregation of polystyrene spheres of radius $a = 10.5$ nm, suspended in a buoyancy-matching mixture of H_2O and D_2O. The amount of salt is chosen in such a way that the aggregation follows the diffusion-limited cluster aggregation (DLCA) regime, resulting in the formation of a percolated network of closely-packed fractal clusters, whose size is roughly monodisperse and of the order of several tens of microns.[10] Typical particle volume fractions range from 10^{-4} to 10^{-3}; more details on the sample can be found in ref. 11.

The concentrated emulsions are formed by water droplets in oil (cyclomethicone) and were prepared using a standard laboratory homogenizer. In order to match the refractive index of the oil phase, the water phase contains 56.25% and 1.25% w/w propylene glycol and NaCl, respectively. The droplets are stabilized by a surfactant (Copolyol, Dow Corning 5225C, at 0.25% w/w); their average size and standard deviation are 1 μm and 0.4 μm, respectively, as determined by optical microscopy. Prior to light scattering measurements, the samples are centrifuged for 15 min at a rate between 1500 and 1900 rpm, in order to eliminate the air bubbles that are inevitably trapped when loading the scattering cell. No significant changes in the droplet size distribution are found after centrifugation, as checked by optical microscopy. Oscillatory rheology measurements exhibit the typical behavior for concentrated emulsions:[12] for frequencies 0.1–100 rad s^{-1}, the elastic modulus G' is essentially frequency-independent and scales as $\phi - \phi_c$, where ϕ is the volume fraction of the dispersed phase and $\phi_c \sim 0.6$ is the critical volume fraction for the fluid–solid or jamming transition. All experiments reported here were done at $\phi = 0.777$.

The micellar polycrystal is formed by a mixture of water and a commercially available triblock-copolymer (Synperonic F108, (ethylene oxide)$_{127}$–(propylene oxide)$_{48}$–(ethylene oxide)$_{127}$, by Serva, used without any further purification), to which a small amount of oil is added (p-xylene, from Aldrich). At low temperature ($T = 4\,^\circ$C), both the poly(ethylene oxide) (PEO) ends and the central poly(propylene oxide) (PPO) section of the block-copolymer are soluble in water. As the

temperature is raised, PPO becomes increasingly hydrophobic and the polymers start forming micelles, whose PPO core is swollen by p-xylene[13] (the purpose of the oil is to increase the refractive index contrast between the micelles and water, in order to obtain a high enough light scattering signal). Depending on the final temperature and the sample composition, different liquid crystalline phases can be obtained. Typically, samples are prepared by thoroughly mixing all components at $T = 4\,^{\circ}\text{C}$ (the system is fluid at this temperature); the temperature is then increased and the sample solidifies. For all experiments reported here, the sample composition is 75.8/22.3/1.9 water/F108/ p-xylene (w/w %), and T is increased from 4 to $30\,^{\circ}\text{C}$ at a rate of about $1\,^{\circ}\text{C s}^{-1}$. Under these conditions, the micelles arrange themselves on a face centered cubic (fcc) lattice, whose cell size is 51 nm, as revealed by small-angle X-ray scattering (SAXS) experiments.[14]

The lamellar gel is formed by closely-packed polydisperse multilamellar vesicles (MLV, characteristic size about 5 μm), whose bilayers are composed of a mixture of cetylpyridinium chloride (CpCl) and octanol (Oct) (CpCl/Oct = 0.95 w/w) diluted in brine ([NaCl] = 0.2 M) at a weight fraction of 16%.[15] The smectic periodicity of the lamellae is 13 nm, as measured by small-angle neutron and X-ray scattering.[16,17] An amphiphilic block-copolymer (Synperonic F68, (ethylene oxide)$_{76}$–(propylene oxide)$_{29}$–(ethylene oxide)$_{76}$, by Serva) is added to the system at a copolymer-to-bilayer weight ratio of 0.8. The central hydrophobic section of the copolymer adsorbs to the bilayers, while the hydrophilic ends are swollen in water and decorate the membrane. Upon copolymer addition, a marked and continuous hardening of the system is observed, resulting in a so-called lamellar gel.[16–18] Similarly to the micellar polycrystals, lamellar gels exhibit a transition from a fluid state to solid-like behavior when increasing T from about 4 to $20\,^{\circ}\text{C}$.

For all systems, we define the sample age t_w as the time elapsed since the sample was first quenched in the jammed phase. For the colloidal gels, the jamming is due to the growth of the effective volume fraction as the fractal cluster size increases, eventually leading to gelation; we thus identify $t_w = 0$ with gelation, as detected by the arrest of the shift towards smaller scattering vectors of the peak in the scattered intensity vs. q.[10,11] We recall that the concentrated emulsions are centrifuged prior to scattering measurements. Since the stress induced by centrifugation provides a means to erase any memory of the sample's previous history,[19–22] for these samples we take t_w as the time elapsed since the end of centrifugation. Finally, for both the micellar polycrystals and the lamellar gels, the jamming transition is controlled by varying T and thus t_w is defined as the time elapsed after the temperature (inverse) quench. For all systems, the uncertainty in the determination of the sample age is of the order of a few tens of seconds, small compared to the typical values of t_w that can be as long as several tens of days.

We use dynamic light scattering as a non-invasive technique to probe the sample dynamics: by measuring the time autocorrelation function of the fluctuations of the scattered intensity, the dynamic structure factor $f(q,t)$ can be obtained via the Siegert relation.[23] Here, $q = 4\pi n \lambda^{-1} \sin(\theta/2)$ is the scattering vector, with n the refractive index of the medium, λ the in vacuo laser wave length, and θ the scattering angle. The dynamics of the fractal gels and that of the concentrated emulsions were studied for a wide range of scattering vectors q ($1.5 \times 10^{-2}\ \mu\text{m}^{-1} < q < 1\ \mu\text{m}^{-1}$) by using ultralow angle multispeckle DLS. The set-up, which is described in detail in ref. 8, is based on a charge coupled device (CCD) detector; it allows us to measure relaxation processes as long as a few tens of hours on length scales as large as several tens of microns. For the micellar polycrystals and the lamellar gels, we used a combination of conventional and multispeckle wide-angle DLS in order to access the sample dynamics on time scales ranging from a fraction of microsecond to a few tens of hours, and at scattering vectors between 3.0×10^{-2} and $0.33\ \mu\text{m}^{-1}$ (corresponding to $10^{\circ} < \theta < 150^{\circ}$).

A more complete discussion of the multispeckle technique can be found in ref. 7 and 8; here we simply recall that intensity autocorrelation functions are measured in parallel for several thousands of speckles,[23] or coherence areas, by using a CCD camera and custom designed software. The correlation functions thus obtained are averaged over sets of speckles with the same temporal statistics. For isotropic systems and in the ultralow angle apparatus (colloidal gels), these sets of speckles are associated with rings of pixels centered about the incident beam direction, corresponding to scattering vectors $\boldsymbol{q}$ whose magnitude spans a small interval ($q_0 < q < q_0 + \Delta q$, with $\Delta q/q_0 \approx 0.01$), and whose azimuthal angle varies from 0 to 2π. For the concentrated emulsions studied by ultralow angle light scattering, the averaging is done over small solid angles $\Delta\Omega$ centered about scattering directions corresponding to $\boldsymbol{q}$ either parallel or perpendicular to the direction of

the acceleration imposed on the sample during centrifugation. Finally, for wide angle measurements (micellar polycrystals and lamellar gels), the averaging is done over a small solid angle $\Delta\Omega$ centered about a given scattering direction lying in the scattering plane. Thanks to the speckle averaging procedure, the measurement time can be as short as the longest relaxation time of the system, several thousand times less than in traditional DLS. It is therefore possible to measure very slow dynamics and to fully characterize their time evolution. Moreover, multispeckle DLS directly yields ensemble-averaged correlation functions, so that no special precautions are needed to investigate non-ergodic samples such as the jammed systems presented here. On the contrary, special care was taken for the traditional DLS measurements, since the samples studies in this paper are non-ergodic on the time scale of a conventional light scattering experiment. Therefore, the measured time-averaged intensity autocorrelation function is not simply related to the desired ensemble-averaged dynamic structure factor $f(q,t)$ and special techniques are required to collect and interpret the data.[24] We used the so-called "brute force method", where raw correlation function are averaged over several tens of runs (typically 100) prior to normalization, the sample being rotated or translated between every run to probe different scattering volumes.

III   Results

In this section we present the multispeckle and conventional DLS measurements on the four systems we investigated: colloidal fractal gels, concentrated emulsions, micellar polycrystals, and lamellar gels. For each system, we first describe and briefly discuss the fast dynamics, then we report the experimental results for the slow dynamics and its evolution with sample age.

Colloidal fractal gels

A detailed study of the fast and slow dynamics of DLCA colloidal fractal gels, as well as of their evolution with age, has been published in ref. 11 and 25. In view of the striking similarities with the other systems described here, we recall briefly the main findings of these works. The dynamic structure factor $f(q,t)$ exhibits a two-step decay. The faster relaxation has been studied by conventional DLS:[25] at short times, it can be very well described by a stretched exponential, $f(q,t) = \exp(-D_b q^2 t^b)$, with a stretching exponent $b = 0.7$ and a q^2 dependence that is the signature of the diffusive nature of the fast dynamics. This initial decay is followed by a plateau, whose height decreases with increasing q. The physical origin of this dynamics is the thermally excited internal elastic modes of the gel, which span a wide range of length scales, due to the fractal morphology of the system: Krall and Weitz developed a model which allows the elastic properties, namely the elastic modulus, to be obtained from the DLS data. Note that no significant age dependence is found for the short time dynamics. At time scales of several thousands of seconds, much longer than those accessible to traditional DLS, multispeckle experiments[11] have revealed, totally unexpectedly, the existence of a second, ultraslow relaxation, which leads to the full decay of the correlation function. The complete loss of correlation of the scattered light indicates that rearrangements occur on length scales of the order of $2\pi/q$; these rearrangements thus involve displacements over distances as large as tens of microns, comparable to the cluster size. The slow relaxation has the very peculiar shape $f(q,t) \propto \exp[-(t/\tau_s)^p]$, with $p \approx 1.5$ and a very unusual q dependence of the characteristic decay time: $\tau_s \sim q^{-1}$. Because the stretching exponent is larger than one, the final relaxation is faster than exponential; in the following we shall refer to it as a "compressed" exponential and indicate by p the "compressing" exponent. Moreover, we note that the inverse-q scaling of τ_s is in sharp contrast with the q^{-2} scaling typical of a diffusive process, thus ruling out diffusion as a possible mechanism for the slow dynamics. Contrary to the fast dynamics, the slower decay of the dynamic structure factor is found to be strongly dependent on sample age t_w, increasing by almost three orders of magnitude over 10 days. The initial growth of τ_s is approximately exponential, while at large t_w the aging is almost linear ($\tau_s \sim t_w^{0.9\pm0.1}$).

Concentrated emulsions

The short time dynamics of concentrated monodisperse emulsions has been studied by both diffusing wave spectroscopy (DWS)[26] and traditional DLS.[27] At early times ($t < 1\ \mu s$), the dynamics

is dominated by shape fluctuations of the droplets, as revealed by DWS. At longer times, the dynamics crosses over to the subdiffusive (because of hydrodynamic interactions) local motion of the droplets within the cage formed by their neighbors. This motion results in the initial decay of the dynamic structure factor measured by conventional DLS. For concentrated emulsions, the initial relaxation is followed by a well developed plateau that extends over almost all the accessible time delays, until some decay is observed for the longest time delays ($t > 200$ s), in good qualitative and quantitative agreement with the predictions of the extended mode coupling theory. Interestingly, the incipient decay observed at the longest time delay has been ascribed to the deformability of the liquid droplets and to the relaxation of internal stresses built up as the sample is loaded in the cell; moreover, a slow increase of the final relaxation time with sample age has been observed.

To better investigate the slower relaxation of $f(q,t)$ in concentrated emulsions, we performed ultra-low angle multispeckle DLS measurements on a similar (but polydisperse) system. The dynamic structure factors measured simultaneously for several q parallel to the direction of the acceleration imposed by the centrifugation and for a sample age of 300 s are shown in Fig. 1(a). Surprisingly, we find the same behavior as for the colloidal gels: the dynamic structure factor decays with a compressed exponential shape, $f(q,t) \propto \exp[-(t/\tau_s)^p]$, with an average exponent $p \approx 1.50 \pm 0.08$ (the lines are compressed exponential fits to the data; for $f(q,t) < 0.25$, the experimental data are affected by stray light contributions and were not included in the fit). The q dependence of the slow relaxation time is found to be very close to that of the colloidal gels: $\tau_s \sim q^{-0.90 \pm 0.3}$ (see inset), once again ruling out diffusive motion as the physical mechanism responsible for the decay of $f(q,t)$. Interestingly, at small sample ages we find a similar form for the correlation functions measured for q perpendicular to the centrifugation acceleration, with a relaxation time larger than that measured for q parallel. This anisotropy in the dynamics is consistent with the hypothesis that the slow relaxation is related to the internal stress built in as the cell is loaded and centrifuged, similarly to what was noted in ref. 27. Fig. 1(b) shows the age dependence of the characteristics relaxation time τ_s measured at $q = 0.22$ μm^{-1} for samples that were centrifuged for the same time (15 min), but at different rates. As can be seen, τ_s increase dramatically with t_w; similarly to the initial regime of the colloidal gels, the growth is faster than linear, although more data will be needed to better characterize the aging. Interestingly, as a general trend the relaxation time decreases when increasing the centrifugation rate, further suggesting that the slow dynamics is due to the relaxation of built-in stress, which is likely to be higher
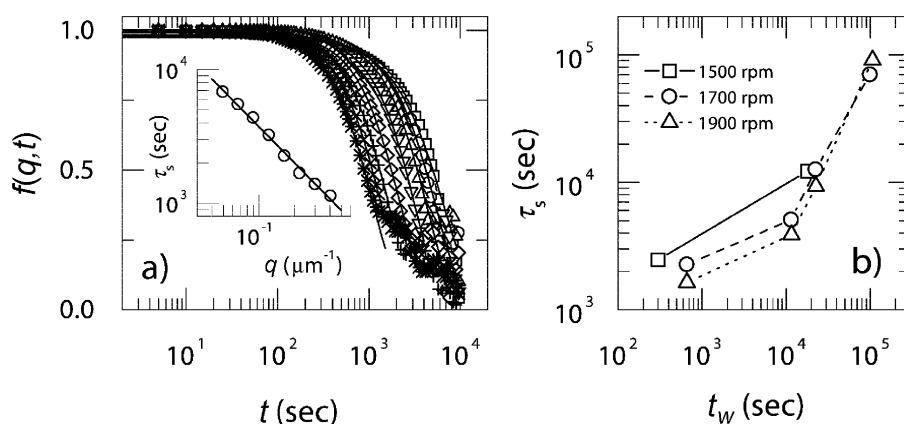

Fig. 1 (a) Dynamic structure factor measured by ultralow angle multispeckle DLS for a concentrated emulsion of age $t_w = 300$ s. Lines are compressed exponential fits to the data (see text), with average compressing exponent $p = 1.50 \pm 0.08$. Inset: q dependence of the characteristic relaxation time of the final decay of $f(q,t)$. The line is a power law fit to the data, yielding an exponent 0.90 ± 0.03, indicative of "ballistic" motion on long time scales. (b) Age dependence of the characteristic time of the final decay of the dynamic structure factor at $q = 0.22$ μm^{-1} for a compressed emulsion. Curves are labeled by the rate at which the samples were centrifuged prior to measurements.

for the samples centrifuged at a higher rate. Additional support is provided by the observation that, after aging, the sample dynamics can be reinitialized by repeating the centrifugation.

Micellar polycrystals

The results of DLS experiments on the micellar polycrystals are shown in Fig. 2 and 3. Fig. 2 shows, for several scattering vectors q, the short-time behavior of $f(q,t)$, measured by conventional DLS. The dynamic structure factor is characterized by a fast relaxation to a plateau, whose height decreases as q grows. We find that a stretched exponential decay to a plateau fits well the fast
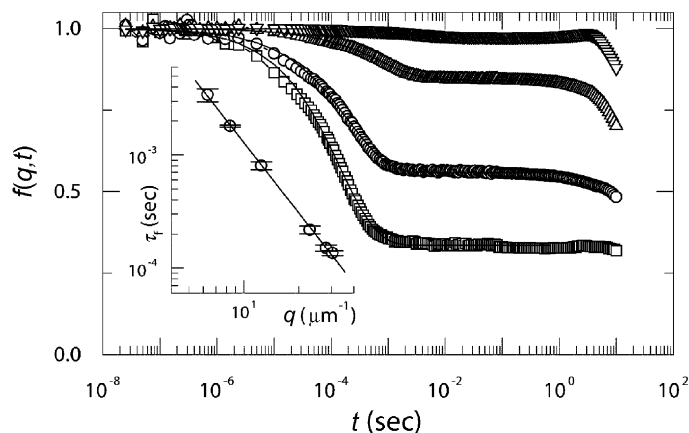

Fig. 2 Initial decay of the dynamic structure factor for a micellar polycrystal. From top to bottom q is 6.2, 12.4, 23.0, and 30.8 μm^{-1}. Lines are stretched exponential fits to the data, with an average stretching exponent of 0.64 ± 0.02. Inset: q dependence of the fast relaxation time of $f(q,t)$. The straight line is a power-law fit to the data, with an exponent 2.07 ± 0.04 that demonstrates the diffusive nature of the fast relaxation.
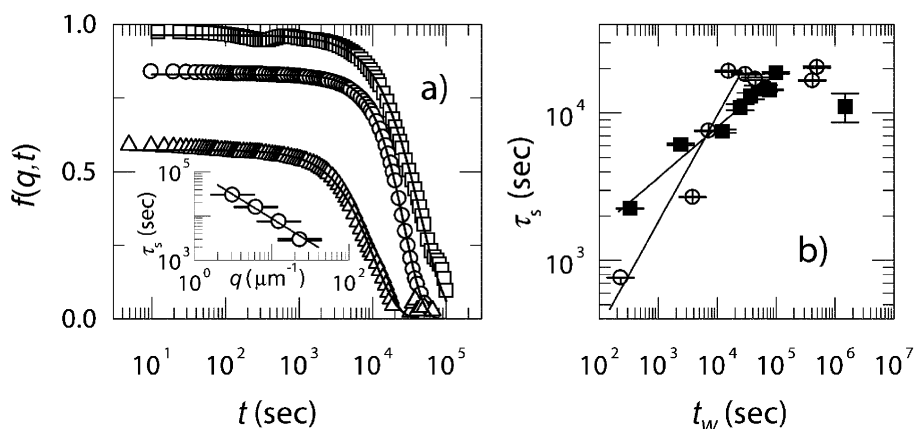

Fig. 3 (a) Final decay of the dynamic structure factor measured by multispeckle DLS for a micellar poly-crystal of age $t_w \approx 6 \times 10^6$ s. Lines are compressed exponential fits to the data, with compressing exponent p. From top to bottom q and p are 5.9, 12.4, and 20.9 μm^{-1}, and 1.3, 1.7, and 1.3, respectively. Inset: q dependence of the characteristic relaxation time of the final decay of $f(q,t)$ for a sample with $t_w \approx 1.5 \times 10^6$ s. The line is a power law fit to the data, yielding an exponent 1.08 ± 0.08. (b) Age dependence of the slow relaxation time of a micellar polycrystal. Solid squares and open circles refer to two series of measurements on the same sample, which was remelted after the first series. The lines are power law fits to the initial growth of τ_s, yielding an exponent of 0.35 (squares) and 0.72 (circles), respectively. For $t_w \geqslant 2 \times 10^5$ s the slow relaxation time tends to saturate.

relaxation of the dynamic structure factor: $f(q,t) = \exp[-(t/\tau_f)^b] + B$, with the same stretching exponent $b = 0.64 \pm 0.02$ for all q (solid lines in Fig. 2). The q dependence of the relaxation time τ_f extracted from the fit is shown in the inset of Fig. 2 on a double logarithmic plot. (Note that data at different q are collected sequentially and therefore for different sample ages. Although *a priori* aging effects cannot be ruled out, we stress that no age dependence of the short time dynamics is observed, as checked by repeating measurements at the same scattering vector for ages ranging from a few minutes to several weeks). As shown by the power law fit (solid line), the relaxation time scales as q^{-2}, thus indicating that the fast relaxation results from a diffusive process, which we identify by the thermal motion of the micelles around their equilibrium position in the crystalline structure. Given the q^{-2} dependence of τ_s, an effective short-time collective diffusion coefficient D_b can be defined through $D_b = (q^2\tau_f)^{-1}$. We find $D_b = 8.4 \pm 0.4 \times 10^{-8}$ cm^2 s^{-1}, a value close to $D = 1.2 \times 10^{-7}$ cm^2 s^{-1}, the self diffusion coefficient calculated for an isolated micelle (the radius $R = 18$ nm of a micelle has been estimated by assuming that micelles are closely packed in the fcc unit cell). This agreement testifies further to the diffusive origin of the first relaxation of the dynamic structure factor. It is worth noting that a similar diffusive fast relaxation was observed in the past for triblock copolymers in a selective solvent,[28,29] a system very similar to the micellar polycrystals studied here. However, the first decay reported in ref. 28 and 29 is a simple exponential, while we find a stretched exponential behavior. This difference may stem from a more heterogeneous environment experienced by the p-xylene-swollen micelles compared to the binary systems described by Nyström *et al.* and Raspaud *et al.* In fact. SAXS experiments[14] on F108/ water crystalline phases show broader Bragg peaks when the micelles are swollen by p-xylene, suggesting that there may be local variations of the unit cell size. Moreover, we find variations of the order of 10% in the Bragg peaks position when probing different volumes of the same sample, further suggesting the existence of inhomogeneities. Because of these variations, the microscopic environment explored by the micelles in their thermal motion would be somehow heterogeneous, thus leading to a wider spectrum of relaxation times and hence to the stretched exponential behavior.

At the largest delays probed by conventional DLS ($t = 1 - 10$ s) the data, although very noisy, hint at the beginning of a second decay of the dynamic structure factor. Since conventional DLS does not allow data to be collected efficiently and reliably at such unusually large time delays, we turned to multispeckle DLS to better investigate the second relaxation. Fig. 3(a) presents $f(q,t)$ measured at various q vectors, for a sample age $t_w \approx 6 \times 10^6$ s.[30] We find that on very long time scales $f(q,t)$ decays completely to zero, revealing that even though the sample is a crystalline solid, ultraslow rearrangements do take place, eventually leading to the loss of correlation of the scattered light. These rearrangements occur on length scales of the order of $2\pi/q$; therefore they involve displacements over distances as large as a couple of microns, much larger than the crystal unit cell size. We thus identify them as rearrangements of the texture of the polycrystals, *i.e.* with the motion of defects such as dislocations and grain boundaries. Remarkably, we find here the same very peculiar behavior of $f(q,t)$ as for the fractal gels and the compressed emulsions. In fact, the final relaxation of the dynamic structure factor can be fit well by a compressed exponential $\exp[-(t/\tau_s)^p]$, with a compressing exponent p larger than 1 and close to 1.5 ($1.3 < p < 1.7$, no systematic q dependence being observed). Moreover, the slow relaxation time τ_s exhibits the same unusual q^{-1} dependence as for the previous systems, (see inset of Fig. 3(a)), thus ruling out diffusion as a possible physical mechanism originating the slow dynamics.[30]

For the colloidal gels[11] and for the concentrated emulsions, as well as for other soft glassy materials[22,31] ultraslow dynamics was found to be associated with aging. For the micellar polycrystals, we investigate aging effects by performing a series of multispeckle DLS measurements at the same scattering vector ($q = 12.4$ μm^{-1}) during the aging of the sample. All dynamic structure factors measured at different ages are found to exhibit the same compressed exponential final relaxation; however the characteristic time τ_s evolves with age. Fig. 3(b) shows on a double logarithmic scale the time evolution of τ_s for two independent series of measures on the same sample, which was melted and re-solidified after the first series. As can be seen, τ_s initially increases by about one order of magnitude, before saturating for $t_w \geq 2 \times 10^5$ s. The initial growth of τ_s appears to be poorly reproducible, possibly because of a great sensitivity to the exact conditions under which the sample is quenched to the solid phase. Nonetheless, for all measurements presented here and for samples of slightly different compositions (data not shown), the aging is

sublinear: a power law fit to the data yields an exponent between 0.4 and 0.7. Both the crossover time to the saturation regime and the magnitude of τ_s at large t_w, on the contrary, appear to be reasonably well reproducible. Further measurements will be necessary to better characterize the initial regime of the aging.

Lamellar gels

We now turn to the experimental results for the lamellar gels. Strikingly, we find that the dynamics is very similar to that of the previous systems, suggesting the generality of the behavior observed for these jammed materials. In fact, the dynamic structure factor exhibits a two-step decay, whose fast relaxation is diffusive-like and age-independent, while the final, slow relaxation is faster than exponential, non-diffusive, and slows down as the sample ages. Fig. 4(a) shows a typical dynamic structure factor measured at $q = 24.2$ μm^{-1} for a lamellar gel at age $t_w = 2400$ s. The curve was obtained by overlapping both conventional and multispeckle DLS data. The fast dynamics is presumably due to the thermally activated fluctuations of the membranes. For oriented samples, (*i.e.* with a unique orientation $\boldsymbol{n}$ for the lamellae), the description of the fluctuations of the membranes is well established, both theoretically and experimentally.[32,33] The initial decay of the dynamic structure factor for a lamellar gel phase can be obtained by averaging the signal for oriented samples over the different lamellae orientations in space.[34] Leng *et al.* show that the initial decay can be approximated by

$$f(q,t) = \frac{C}{1 + t/\tau_f} + B. \tag{1}$$

Here $\tau_f = \nu G q^{-2}$ is closely related to the characteristic time for a layer compression wave at wave vector $\boldsymbol{q}$ oblique with respect to $\boldsymbol{n}$ (baroclinic mode, characteristic time $\tau_B = \nu G|\boldsymbol{q} \wedge \boldsymbol{n}|^{-2}$), where G is the compression modulus of the smectic and ν is a dissipative parameter related to the shear viscosity. We find that the fast relaxation of the dynamic structure is well fit by eqn. (1)), thus allowing us to quantitatively obtain the characteristic time τ_f. The q dependence of τ_f is shown in the inset of Fig. 4(a): τ_f scales as q^{-2}, in very good agreement with the analysis recalled above; moreover, it is age-independent, showing that, similarly to the case of the other systems, the first decay of $f(g,t)$ reflects the short-time diffusive motion of the scatterers which is not affected by
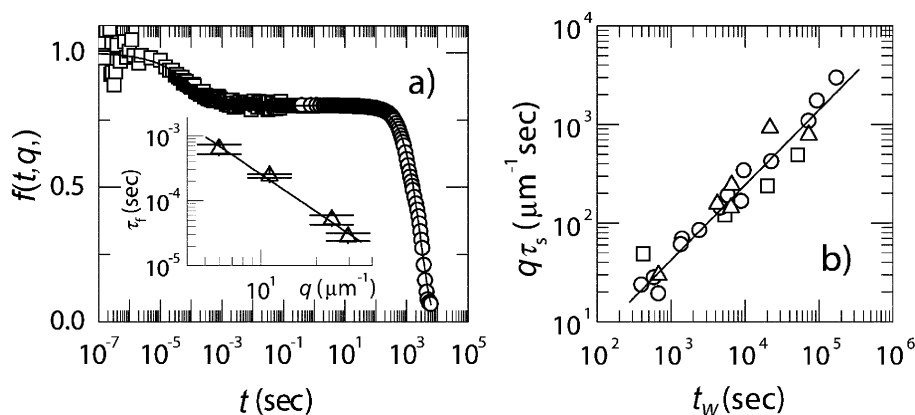

Fig. 4 (a) Dynamic structure factor for a lamellar gel. Data are obtained by combining both conventional (squares) and multispeckle (circles) measurements. The line is a fit to the data resulting from the sum of the initial decay eqn. (1) and a compressed exponential final relaxation with $p = 1.3$. Inset: q dependence of the characteristic relaxation time of the initial decay of $f(q,t)$. The line is a power law fit to the data, yielding an exponent 1.92 ± 0.13, indicative of the diffusive nature of the fast dynamics. (b) Double logarithmic plot of the product $\tau_s q$ *vs.* sample age t_w, where τ_s is obtained from the compressed exponential fit of the final decay of $f(q,t)$. Data were collected at $q = 6$ (triangles), 11.2 (squares), and 24.2 μm^{-1} (circles). All data fall onto a straight line with slope $\mu = 0.77$, thus demonstrating both the q^{-1} scaling of τ_s and the sublinear power law growth of the relaxation time with sample age.

aging. We find a fast diffusion coefficient $D_b = (\nu G)^{-1} = (4.40 \pm 0.23) \times 10^{-7}$ cm^2 s^{-1}, a numerical value consistent with the theoretical expectation.[16,32] The final decay of the dynamic structure factor can be fit by the same compressed exponential function $\exp[-(t/\tau_s)^p]$ as for the colloidal gels, the compressed emulsions, and the micellar polycrystals, with a compressing exponent once again close to 1.5: $p = 1.46 \pm 0.18$ (the fit is shown as a solid line on Fig. 4(a)). Similarly to the other systems, we find that for the lamellar gels τ_s scales as q^{-1} and the dynamics slows down with increasing sample age. To show both the q^{-1} scaling and the aging behavior, we plot the product $q\tau_s$ as a function of t_w in a double logarithmic plot in Fig. 4(b). The different symbols refer to data taken at different q vectors and/or after melting and re-solidifying the sample. All the experimental points fall on the same master curve, thus indicating that indeed $\tau_s \sim q^{-1}$, as well as demonstrating the good reproducibility of the lamellar gel slow dynamics. Moreover, over the whole range of t_w investigated, the data can be fit by a power law $\tau_s \sim t_w^\mu$ with an aging exponent $\mu = 0.77 \pm 0.04$, indicating sublinear aging behavior.

IV Discussion

Ultraslow dynamics

The most striking feature found in the experiments described above is the existence of an ultraslow, "compressed" exponential relaxation of $f(q,t)$, with a characteristic time $\tau_s \sim q^{-1}$. Remarkably, the same behavior is observed for systems as diverse as colloidal gels, concentrated emulsions, micellar polycrystals and lamellar phases. In glassy systems, a two-step decay of $f(q,t)$ is a common feature when approaching the glass transition; experimentally, it has been observed in soft disordered systems such as dense colloidal suspensions,[4,35] concentrated micelles,[36] and polymer gels.[37] It is also characteristic of "hard" disordered materials: for example, it has been described both experimentally and theoretically in spin glasses[6] and in simulations of Lennard-Jones glasses.[38] The commonly accepted physical picture is that the motion of a particle in a disordered, glass-like material is constrained by the "cage" constituted by its neighbors. On short times, scatters diffuse nearly freely within the cage, yielding the initial fast decay of $f(q,t)$. On longer time scales, the dynamics is frozen, until the scatterer escapes from the cage, yielding the final decay of the dynamic structure factor. Since the long term dynamics is dictated by the cage-escape process, the long-time motion is subdiffusive and the decay of the correlation function is slower than exponential. Indeed, both theoretical works and experiments have shown stretched exponential,[39] power-law,[40] or logarithmic decays[36,41] as the final relaxation (or α decay) of the dynamic structure factor.

On the contrary, the final decay of $f(q,t)$ reported in this paper is faster-than-exponential, and the q^{-1} scaling of τ_s rules out diffusive or subdiffusive motion; therefore it cannot be explained in the framework of the cage-escape picture. Additionally, in previous works the final decay was observed when approaching the glass (or jamming) transition from the fluid side, while no complete relaxation on experimentally accessible time scales has been reported for samples deep in the glass phase. This is in sharp contrast with the experiments presented here, where a complete relaxation of the dynamic structure factor is observed even for fully developed solids. Therefore, a different approach is needed to account for these unusual dynamics.

We start by noting that the slow relaxation depends only on the product $x \equiv qt$, rather than on $\boldsymbol{q}$ and t separately, as indicated by the same compressed exponential relaxation shape at all $\boldsymbol{q}$ (we recall that the compressing exponent p is constant within experimental errors) and by the $\tau_s \sim q^{-1}$ scaling. Therefore, $f(q,t) = f(x) = \exp[-(xV_0)^p]$, where $V_0 = (q\tau_s)^{-1}$ represents a characteristic velocity. This peculiar dependence is the hallmark of "ballistic" motion and rules out diffusion: on length scales up to $2\pi/q$, the scatterer displacement grows linearly with time, rather than as $t^{1/2}$. (Note that this ultraslow, large length scale ballistic motion should not be confused with the fast ballistic motion that can be observed in colloidal systems at very short times and on very small length scales, e.g. in DWS experiments that probe the free-fly dynamics before the onset of diffusive-like motion). Under these conditions, the shape of the correlation function is related to the scatterers' velocity-distribution function $P(\boldsymbol{V})$ via[23]

$$f(\boldsymbol{x}) = \int \mathrm{d}^3 V P(\boldsymbol{V}) \exp(i\boldsymbol{x} \cdot \boldsymbol{V}). \tag{2}$$

For the concentrated surfactant phases and the colloidal gels, we expect the scatterers' motion to be isotropic, since the only symmetry-breaking field, gravity, is too weak to affect the dynamics, either because of the large modulus of the samples ($G' \sim 10^2$ and 10^4 Pa for the lamellar gels and the micellar polycrystals, respectively), or due to the buoyancy matching (for the tenuous colloidal gels). For the concentrated emulsions, on the contrary, the direction of the acceleration imposed during the initial centrifugation breaks the rotational symmetry, and thus the dynamics depends on the orientation of q, as discussed in Section III. In the following, we first calculate $P(V)$ for the isotropic samples, and then we show that the same asymptotic behavior is also obtained for the components of the velocity parallel and perpendicular to the centrifugation direction, for the concentrated emulsions.

Following ref. 23, we rewrite the integral in eqn. (2) using polar coordinates and integrate over the angular variables, obtaining

$$f(x) = \int_0^\infty \mathrm{d}V W(V) \frac{\sin(xV)}{xV}, \tag{3}$$

where $W(V)\mathrm{d}V = 4\pi V^2 P(V)\mathrm{d}V$ is the probability that the modulus of the velocity lie between V and $V + \mathrm{d}V$. By a Fourier sine transformation of eqn. (3), we obtain

$$W(V) = \frac{2V}{\pi} \int_0^\infty \mathrm{d}x\, x f(x) \sin(xV). \tag{4}$$

Historically, eqn. (4) has been used to measure the speed distribution for diluted gas particles[42] and motile organisms such as *E. Coli* bacteria.[43] In our case, we note that $f(x) = \exp[-(xV_0)^p]$ is the Fourier transform (the characteristic function, in the language of the theory of probability) of the Levy stable law $L_{p,0}$, which is defined by:[44]

$$L_{p,0}(V/V_0) = \frac{V_0}{2\pi} \int_{-\infty}^\infty \mathrm{d}x \exp(\mathrm{i}xV)f(|x|)$$
$$= \frac{V_0}{\pi} \int_0^\infty \mathrm{d}x \cos(xV)f(x). \tag{5}$$

From eqn. (4) and (5) we obtain

$$W(V) = -\frac{2V}{\pi}\frac{\partial}{\partial V} \int_0^\infty \mathrm{d}x f(x) \cos(xV)$$
$$= -\frac{2V}{V_0}\frac{\mathrm{d}}{\mathrm{d}V} L_{p,0}(V/V_0), \text{ or}$$
$$W(\tilde{v}) = -2\tilde{v}\frac{\mathrm{d}}{\mathrm{d}\tilde{v}} L_{p,0}(\tilde{v}), \tag{6}$$

where we have introduced the normalized velocity $\tilde{v} = V/V_0$. The Levy stable law $L_{p,0}$ is characterized by an asymptotic power-law decay: $L_{p,0}(\tilde{v}) \sim \tilde{v}^{-(p+1)}$. Therefore, eqn. (6) predicts

$$W(\tilde{v}) \sim \tilde{v}^{-(p+1)} \tag{7}$$

for large $\tilde{v}$, as shown in Fig. 5 for $p = 1.5$. We note that if the compressing exponent p in the dynamic structure factor is smaller than 2, the corresponding distribution eqn. (6) has a diverging variance; on the contrary, for $p = 2$ the dynamic structure factor has a gaussian form ($f(q,t) \sim \exp[-q^2 t^2 V_0^2]$), and corresponds to a gaussian distribution of the components of the scatterers' velocity, as observed, for example, for diluted gases.[42]

To calculate the velocity distribution for the anisotropic samples, such as the centrifuged concentrated emulsions, we start by recalling that a homodyne DLS measurement is sensitive only to the component of the displacement parallel to the scattering vector q. Therefore, if q is oriented along the direction of the centrifugation acceleration (which we denote by the subscript "$\parallel$": $q = q_\parallel$), eqn. (2) yields

$$f(x_\parallel) = \int \mathrm{d}V_\parallel \exp(\mathrm{i}x_\parallel V_\parallel) \int \mathrm{d}_2 V_\perp P(V), \tag{8}$$
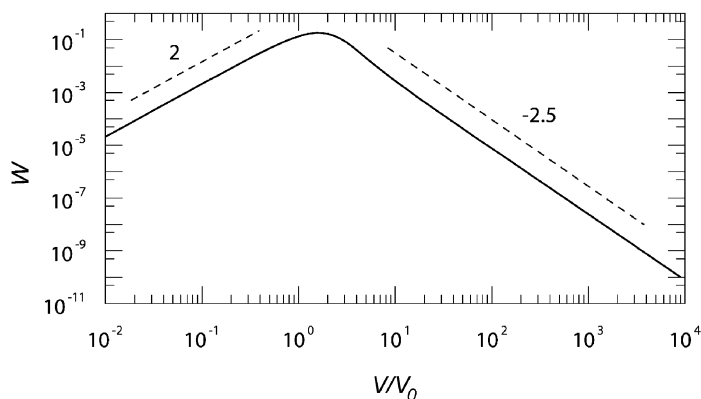
Fig. 5 Probability distribution $W(V)$ for the modulus of the velocity, calculated from the Levy law $L_{p,0}$ as indicated in the text, corresponding to a compressed exponential relaxation of $f(q,t)$ with compressing exponent $p = 1.5$.

with $x_\parallel = q_\parallel t$ and where the subscript "$\perp$" refers to the plane perpendicular to $q_\parallel$. We introduce $P_\parallel(V_\parallel)$, the probability distribution of the component of the velocity parallel to the centrifugation acceleration, obtained by integrating $P(V)$ over all values of the perpendicular components: $P_\parallel(V_\parallel) = \int d_2 V_\perp P(V)$. Eqn. (8) can then be Fourier transformed with respect to $V_\parallel$, yielding

$$P_\parallel(V_\parallel) \propto \int dx_\parallel \exp(ix_\parallel V_\parallel) f(x_\parallel) \sim V_\parallel^{-(p+1)}. \tag{9}$$

where we have used the definition of the Levy law $L_{p,0}$ eqn. (5) and its asymptotic behavior for large V. Similar arguments can be developed for the case where q is perpendicular to the centrifugation direction. Therefore, eqn. (9) shows that, for the anisotropic samples, the same wide distribution is found for the components of the velocity as for the modulus of the velocity for the isotropic samples.

The question naturally arises as to the physical origin of the ballistic ultraslow motion and of the wide distribution of velocities inferred from the shape and q dependence of the dynamic structure factor. As a starting point, let us recall that, for the colloidal gels, the final relaxation of $f(q,t)$ was ascribed to the local deformation of the elastic network due to the syneresis of the gel.[11] Although no syneresis is observed for the other materials studied here, we propose that the same physical mechanism as for the colloidal gels, *i.e.* the deformation under the action of internal stresses, is responsible for the final decay of the dynamic structure factor. Indeed, several observations point to the central role of stress relaxation in the dynamics of these jammed systems. Recent linear rheology measurements on the lamellar gels[15] show that the characteristic time of the mechanical response of the material evolves with age following exactly the same law as τ_s, which is measured by multispeckle DLS. Since rheology probes the response to an (external) stress, this concordance supports the key role of stress relaxation in the evolution of disordered systems, in particular in the aging process. Moreover, as discussed in Section III, for the concentrated emulsions the dynamics is faster in the direction of the centrifugation stress, along which most of the internal stress has been presumably built in. Finally, we observe that internal stress is certainly built into the micellar polycrystals during crystallization, due to the rapid growth of randomly oriented crystallites during the (inverse) temperature quench.

From a general point of view, without specifying the microscopic origin of the internal stress, we can draw a simplified scenario, whose basic ingredients were first introduced for the colloidal gels,[11] that seems to be sufficient to explain the results observed for all the systems investigated. In this framework, we assume that the dynamics is due to the action of randomly distributed, internal stress sources on the sample, whose response is that of an elastic solid in the linear regime. We denote by $u(t)$ the deformation field induced by a stress source on a point at a distance $r(t)$ from the source and we assume that the number density of the stress sources is small, so that their average

distance is much larger than the largest length scale probed by light scattering. Under such conditions, the time variation of $r(t)$ is negligible and will be dropped in the following. To calculate the r dependence of the displacement field, we note that, in the spirit of a multipole expansion, $u(t)$ can be developed as a sum over powers of $1/r$, whose leading term is expected to be proportional to $1/r^2$ (dipolar contribution), since the $1/r$ term corresponds to the deformation induced by a point-like external force,[45] and here no external forces are acting on the sample. Thus, we retain only the leading term in the multipolar expansion and introduce, for the sake of generality, an effective exponent α:

$$u(t) = A(t)r^{-\alpha}, \tag{10}$$

with $\alpha \approx 2$ (deviations from $\alpha = 2$ may be due to the contribution from the scatterers closer to a stress source, for which the dipole approximation breaks up, and to higher-order multipole terms).

The factor $A(t)$ in eqn. (10) accounts for any time variation of the strength of a stress source and is crucial to explain the slow dynamics of colloidal gels. In fact, at a given scattering vector the elastic deformation due to a stress source propagates through the sample on time scales of the order of the characteristic time of the fast dynamics τ_f, i.e. almost instantaneously compared to the typical time scale τ_s of the final relaxation of $f(q,t)$. Therefore, the slow dynamics cannot be due to the propagation of the elastic deformation, but rather to the time evolution of the strength of the stress centers. Since multispeckle DLS indicates that the motion is ballistic ($u(t) \propto t$), we deduce $A(t) \propto t$, at least over time scales comparable to the relaxation time of $f(q,t)$. Although a more complicated time dependence of $A(t)$ on longer time scales is conceivable, given the very slow aging of the samples it appears reasonable that on intermediate time scales $A(t)$ varies approximately linearly, yielding the "ballistic" nature of the dynamics measured by light scattering. From eqn. (10) and the linear time dependence of $A(t)$ we obtain the scaling $V \sim r^{-\alpha}$. Moreover, the assumption that the stress sources be randomly distributed in space yields $dN \propto r^2 dr$, where dN is the number of stress sources at a distance between r and $r + dr$ from any given point. By combining the r dependence of V and that of dN, we obtain

$$\frac{dN}{dV} \sim \frac{1}{V^{3/\alpha+1}}. \tag{11}$$

Since dN/dV is proportional to $W(V)$, a comparison between eqn. (7) and (11) yields $p = 3/\alpha \approx 1.5$, in very good agreement with the experimental results, thus providing convincing evidence that this simple phenomenological model accounts for the very unusual slow dynamics reported here. We note that, for the concentrated emulsions and the surfactant systems, the ballistic dynamics could also result from overdamped motion, rather than a linear variation of the strength A of the stress sources. Overdamped motion would be due to the viscous drag acting on elements (such as dislocations, for the micellar polycrystals or the lamellar gel) that interact through elastic forces. In this respect, ballistic dynamics with an intriguingly similar power law distribution of velocities was reported in a simulation of the overdamped flow of elastically interacting dislocations in a single ice crystal under the action of an external stress.[46]

Although the elastic relaxation of heterogeneous internal stresses appears to be the key ingredient to explain the form of the structural relaxation in a wide range of jammed soft materials, for most systems a detailed description of the microscopic origin of the dynamics is still lacking. For the colloidal gels, Bouchaud and Pitard introduced a model for local rearrangements.[47] In this model, it is assumed that at a microscopic level, local irreversible collapses of particles happen randomly in time and space in the system, due to the continuing process of aggregation (new bonds can be formed when thermal motion of dangling ends or floppy loops brings particles to contact). At each collapsing site, this process will induce a dipolar force and, at equilibrium, the modulus of the displacement field $u(r)$ induced by such dipoles is found to decay as the inverse squared distance to the collapsing site: $u(r) \propto (P_0/k)(1/r^2)$, where P_0 is the modulus of the dipolar force and K is the elastic modulus of the gel. Moreover, the strength of each dipole resulting from a microcollapse is assumed to have a linear time dependence, reflecting ballistic motion, until it saturates when the microcollapse is complete. Therefore, one must introduce a linear time dependence in $P_0(t)$ and sum over many random collapse events. The analytical form for the dynamic structure factor can be worked out in this microscopic model, and is in agreement with the experiments, i.e. $f(q,t) \sim \exp[-(qtV_0)^{1.5}]$.

For the other systems, the identification of the microscopic events driving the dynamics remains at present conjectural. In the case of concentrated emulsions and lamellar gels, the dynamics may be due to a very heterogeneous initial distribution of stresses that relaxes due to the soft contacts between spheres or thanks to local topological rearrangements similar to those observed in foams.[48] For the micellar crystals, the driving mechanism could be the elastic relaxation of topological defects (created during the inverse quench of the sample) such as dislocations or grain boundaries, that undergo overdamped motion similar to the dislocations in the system described by Miguel *et al.*, although under the action of internal rather than external stress.

Aging

A shared feature of all the jammed systems investigated here is the slowing down of the final decay of $f(q,t)$ with sample age. Aging is a common feature in glassy systems, and has been interpreted quite generally as an increasingly slower relaxation towards equilibrium as the system spends more and more time in the metastable states it visits (the energy of such states becoming increasingly lower).[6] A number of models based on this picture have been developed and all lead to linear or sublinear dependence of the relaxation time with respect to the waiting time. In the materials studied here, however, the aging behavior is found to vary significantly from one system to another. In fact, the age dependence of τ_s ranges from sublinear (lamellar gels, Fig. 4(b)), to sublinear followed by a saturation regime (micellar polycrystals, Fig. 3(b)), to faster-than-linear (concentration emulsions, Fig. 1(b); initial regime of the colloidal gels, before the onset of the quasi-linear regime). Similarly varied aging behavior has also been observed for other soft systems.[21,22,31] The interpretation is hence quite delicate, and it is difficult to identify the metastable states visited by the system during its evolution towards equilibrium. Moreover, different microscopic mechanisms are likely to take place in the different systems.

With respect to the simple phenomenological model developed in this paper, the slowing down of the dynamics can be explained either by a decrease in the rate of change of the stress source strength $A(t)$ as the sample becomes older, or by a change in the number of active stress sources. Indeed, we note that the relaxation of stresses in the material through local reorganizations may lead in turn to the formation of new stress sources with a longer lifetime, giving rise to a longer relaxation time. This can be illustrated for the colloidal gels, where microcollapses of particles induce stresses on the non-collapsed regions of the sample; subsequent microcollapses in these regions may then harden the local elastic network and thus slow down the relaxation towards equilibrium. In the framework of the microscopic model of Bouchaud and Pitard, an expression for the rate of creation of microcollapses with age can be found, which results in a rapid increase in τ_s with t_w, followed by a sublinear aging regime, similar to what is observed experimentally.

As a final remark, we note that the saturation of the aging observed for the micellar polycrystals suggests that a steady state is reached, in which stress sources are created (presumably by thermal activation) and annihilated (because of the rearrangement of the polycrystalline texture) at the same rate. Unfortunately, for the other samples τ_s grows to several tens of hours, thus exceeding the current experimental limits of multispeckle DLS. Whether or not a similar steady state is eventually reached also for the other systems remains thus an open question.

V Conclusions

We have studied the dynamics of several jammed soft materials by conventional and multispeckle dynamic light scattering. For all systems, the dynamic structure factor exhibits a two-step decay: while the initial relaxation is indicative of the arrested diffusive motion typically observed in glassy systems, the final decay has a very unusual form. Its compressed-exponential shape and the q^{-1} dependence of its characteristic time can be explained by the ultraslow ballistic motion of the scatterers under the action of internal stresses. Interestingly, the compressing exponent p smaller than 2 is here indicative of a wide distribution of ballistic relaxation times, while the stretching exponents smaller than 1 often observed in glassy systems result from a wide distribution of diffusive or subdiffusive relaxation times.

The dynamics observed here are likely to be a very general feature of disordered, jammed systems. In fact, most disordered systems are prepared by quenching them from the fluid to the solid

phase, so that internal stresses are inevitably built in at the jamming transition. In order to test this hypothesis, more experiments on a wide range of systems, including colloidal glasses, will be needed. The role of internal stress could also be investigated by varying the rate and the depth of the quench in the jammed phase, because deeper and faster quenches will presumably induce larger internal stresses.

Further work will be needed to gain a better understanding of the microscopic mechanisms responsible for the ultraslow dynamics, as well as of the different aging behaviors. An important feature of such a microscopic description is likely to be the spatial and temporal heterogeneity of the dynamics. Indeed, both experimental and theoretical work have highlighted intermittency and spatial inhomogeneity in the dynamics of foams[49] and glasses;[50,51] ongoing experiments on the systems studied in this paper indicate a similar behavior, thus suggesting new fascinating similarities between vastly different jammed systems.

Acknowledgements

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