Ultraslow dynamics and stress relaxation in the aging of a soft glassy system

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Abstract

We use linear rheology and multispeckle dynamic light scattering (MDLS) to investigate the aging of a gel composed of multilamellar vesicles. Light scattering data indicate rearrangement of the gel through an unusual ultraslow ballistic motion. A dramatic slowdown of the dynamics with sample age $t_w$ is observed for both rheology and MDLS, the characteristic relaxation time scaling as $t_w^{\mu}$. We find the same aging exponent $\mu = 0.78$ for both techniques, suggesting that they probe similar physical processes, that is the relaxation of applied or internal stresses for rheology or MDLS, respectively. A simple phenomenological model is developed to account for the observed dynamics.

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The fascinating structural properties of colloidal systems are now richly documented experimentally and, for most, theoretically well understood. Modeling their dynamics remains however more challenging. In particular, the extremely slow dynamics and aging properties of disordered, out-of-equilibrium systems raise puzzling questions. A theoretical approach has been recently proposed by Sollich et al. [1,2], who introduced the notion of soft glassy materials and modeled the glass-like transition and the linear and nonlinear rheology properties of out-of-equilibrium soft systems, with a theory adapted from glasses. Despite the large variety of materials which belong to the soft glassy materials classification (dense emulsions, pastes, foams, gels, ...), the experimental investigations of their out-of-equilibrium properties still remain scarce, mostly because of experimental difficulties.

In this Letter, we study close-packed multilamellar vesicles (MLVs). These systems are typically formed by shearing a surfactant lamellar phase, otherwise relatively flat, above a critical shear rate [3]. Here, a compact arrangement of MLVs is obtained by incorporating an amphiphilic block-copolymer into the surfactant lamellar phase [4]. We show that this system is metastable, as evidenced by the evolution of its dynamics and mechanical properties and we present an experimental investigation of the aging process of this material by means of two independent techniques: dynamic light scattering (DLS) and linear rheology. Both the rheological response function (stress relaxation following a step-strain) and the intensity autocorrelation function, measured by DLS, exhibit a dramatic slowdown of their characteristic relaxation time $\tau$ with sample age $t_w$. In both cases, $\tau$ increases as a powerlaw with age: $\tau \sim t_w^{\mu}$. Remarkably, we find the same aging exponent $\mu = 0.78$ for both rheology and DLS, thus strongly suggesting that the two techniques probe the same physical process. However, an intriguing difference exists in the shape of the relaxation functions. The rheology relaxation function is a stretched exponential with a small stretching exponent $m \approx 0.2$, while the correlation function measured by DLS displays an unusually large stretching exponent $p \approx 1.5$, associated with a $1/q$ dependence of the relaxation time, where $q$ is the scattering vector. We discuss these results in terms of rearrangement of the texture of the sample driven by the relaxation of internal and applied stresses through ballistic motion of the MLVs.

The lamellar phase is constituted by bilayers composed of a mixture of cetylpyridinium chloride (CpCl) and octanol (Oct) (weight ratio CpCl/Oct = 0.95), diluted in brine ([NaCl] = 0.2M) at a weight fraction of 16%. The smectic periodicity of the lamellae is 16 nm, as measured by neutron scattering [5]. The bilayers are decorated by an amphiphilic copolymer, Symperonics F68 by Serva ((EO)$_{76}$ − (PO)$_{29}$ − (EO)$_{76}$, where EO is ethylene oxide and PO is propylene oxide). The copolymer-to-bilayer weight ratio $\Omega$ ranges from 0 to 1.6. Upon copolymer addition, the lamellar structure is preserved but a marked and continuous hardening of the system is observed, resulting in a lamellar gel [5,6]. Polarized light microscopy observation of the gel reveals a texture characteristics of a dense arrangement of MLVs [5]. Additional evidence for the large-scale structure of the bilayers is provided by microscope images of a gel brought in contact with the solvent: as shown in the inset of Fig. 1, detachment of individual MLVs close to the gel/solvent boundary is observed, whose size distribution is relatively narrow (diameter $\approx 5.0 \pm 0.8 \mu m$). In the gel, on the contrary, MLVs have polyhedral shape; a three-dimensional network of flat interfaces, similar to that of a dried foam, separates domains where the lamellae have the same orientation. Refractive index fluctuations at these flat interfaces scatter light; indeed, the light scattered...
intensity decays as \( q^{-3.76 \pm 0.03} \) for \( 3 < q < 31 \, \mu m^{-1} \), a powerlaw behavior characteristic of the scattering from a disordered network of planes \[7\].

We perform both oscillatory and stationary rheological experiments in a Couette geometry with a Paar Physica UDS 200 stress-controlled rheometer, operated in the strain-controlled mode through a feedback loop. All measurements are done in the linear regime. The temperature and time dependency of the elastic modulus, \( G' \), and loss modulus, \( G'' \), of a gel are reported in Fig. 4. At a temperature \( T = 4^\circ C \) the material is a viscoelastic fluid, characterized by a weak complex modulus of the order of 1 Pa whose imaginary part is dominant. A temperature ramp to \( T = 20^\circ C \) increases by several orders of magnitude both moduli. The system presents thereafter the characteristic of a gel: the elastic modulus is about one order of magnitude larger than the loss modulus and is nearly frequency-independent in the range \( 10^{-2} - 10 \, Hz \). The gel thus formed is an out-of-equilibrium system, as shown by the time evolution of \( G' \) and \( G'' \). Indeed, after the formation of the gel both moduli evolve continuously, never reaching a steady value. Figure 4 shows the rapid increase of \( G' \) and \( G'' \) during the temperature ramp, followed by their slow but continuous decrease with time, over a period of 2 days. Interestingly, the time dependence of the moduli is dominated by the variation of the loss modulus, whose relative decrease is always larger than that of \( G' \), consistently with theoretical predictions for the aging of soft glassy materials \[2\]. The temperature dependence of the complex modulus (Fig. 1) is fully reversible. Thus, the thermal treatment allows us to erase any memory of the loading procedure and to perform measurements from a well controlled initial state. We define age \( t_w = 0 \) at the maximum of \( G'' \) (arrow in Fig. 1).

The typical time evolution of the linear step-strain response function, \( G(t, t_w) \), is shown in Fig. 2 for a strain amplitude \( \gamma = 1\% \) \[8\]. The different curves in Fig. 2 correspond to different ages \( t_w \) of the sample: after forming the gel, the sample ages unperturbed during a waiting time \( t_w \) before a step strain is applied. In all cases, on time scales of several hours, a full decay of the stress is obtained. The whole relaxation curve is well described by a stretched exponential function, \( G(t, t_w) = G_0 \exp\left[ -\left( \frac{t - t_w}{\tau_R} \right)^m \right] \), where \( \tau_R \) and \( m \) are the relaxation time and the stretching exponent for rheology, respectively. The data exhibit a dramatic slowdown of the relaxation with sample age, the characteristic time \( \tau_R \) increasing as a powerlaw of \( t_w \): \( \tau_R \sim t_w^\mu \), with \( \mu = 0.78 \pm 0.09 \). However, despite the marked increase of the characteristic time, the relaxation functions measured at different ages have all the same shape, and are thus characterized by the same age-independent stretching exponent \( m \), as demonstrated by the collapse of data taken at different ages onto a master curve when \( G/G_0 \) is plotted against \( (t - t_w)/\tau_R \) (Fig. 3). For the sample \( \Omega = 0.8 \) shown in Figs. 2 and 3, \( m = 0.19 \pm 0.01 \). Qualitatively similar master curves have been obtained with different soft disordered systems \[2\].

To independently probe the aging of the MLVs gels, we use a completely different technique, multispeckle dynamic light scattering (MDLS) \[10\]. A charge-coupled device camera is used as a multi-element detector in place of a phototube on a standard light scattering apparatus. Intensity autocorrelation functions are averaged over several thousands pixels, corresponding to about 500 independent speckles or areas of coherence associated to a small solid angle centered around the direction of a given scattering vector \( q \) (the spread in scattering vector is \( \Delta q/q \simeq 10^{-2} \)). Thanks to the multispeckle technique, the typical measurement duration is reduced to the longest delay in the correlation function, thus allowing
snapshots of the dynamics to be taken, thereby directly probing the aging. Samples are initialized by a thermal treatment equivalent to that performed in the rheology experiments. Figure 4 shows the time evolution of the dynamic structure factor \( f(q, t, t_w) \), measured at \( q = 11.2 \mu m^{-1} \). Except for the initial decay of \( f(q, t, t_w) \), whose characteristic time (of the order of 0.5 msec) is too fast to be measured by MDLS and thus is not visible in Fig. 4B, the dynamics is essentially frozen on time scales up to several thousands seconds. Surprisingly, although the system is solid, a full relaxation of \( f(q, t, t_w) \) is eventually observed, indicating rearrangements on length scales up to 1 \( \mu m \). The relaxation characteristic time increases with age, reaching values as large as \( 10^5 \) sec. Similarly to the rheology response functions, the final relaxation of MDLS correlation functions is well fitted by a stretched exponential: 

\[
 f(q, t, t_w) = A \exp[-(t - t_w)/\tau_L]^p, \]

where \( \tau_L \) depends on both \( q \) and \( t_w \). However, the shape of the correlation functions is very different from that of \( G(t, t_w) \), since for MDLS the stretching exponent \( p \) is always larger than 1: \( p = 1.46 \pm 0.18 \). Such an unusual decay has recently been observed for colloidal gels \[11\] and was associated with a very peculiar \( 1/q \) dependence of the relaxation time. Remarkably, the same dependence is found here, as demonstrated by a plot of \( \tau(t) \) versus age, where data taken at different scattering vectors collapse onto the same master curve (inset of Fig. 4). Aging leads to an increase by more than three orders of magnitude of the relaxation time \( \tau_L \), which scales as \( \tau_L \sim t_w^\mu \), with \( \mu = 0.77 \pm 0.04 \). Strikingly, we find the same age dependency for the relaxation time probed by MDLS and rheology, since both \( \tau_L \) and \( \tau_R \) increase as a powerlaw with \( t_w \), with, within experimental errors, the same aging exponent \( \mu \).

Aging indicates that a significant part of the relaxation takes place on time scales close to the sample age, leading to a nearly linear increase of the characteristic relaxation time with age, a feature common to several glassy materials \[3, 11–13\]. We note that, on the time scale of the experiments presented here, no modification of the structure of the MLVs is observed. Therefore we exclude structural evolution as a driving force for aging. Instead, we propose that the dynamics be due to rearrangements of the texture, driven by the minimization of internal stresses. These rearrangements lead to a hardening of the system, as measured by rheology. Moreover, we point out that internal stresses were found to be responsible for the same unusual dynamics in colloidal gels \[11\]: they certainly exist also in the glassy state of a compact arrangement of soft objects and correspond to excess of stored elastic energy quenched in the disordered structure \[14\]. Further support for our interpretation comes from the fact that identical aging processes are found by MDLS and rheology, where the relaxation of an applied stress is directly measured.

A distinctive feature of the slow dynamics reported here is that the final decay of the dynamic structure factor \( f(q, t, t_w) \) depends uniquely on the product \( x = q(t - t_w) \). This is the hallmark of ballistic motion \[16\], with a characteristic velocity \( \bar{V} = (q\tau_L)^{-1} \). The velocity distribution function of the scatterers can be obtained from the shape of \( f(x) \). In the case of isotropic motion, the probability \( W(V) \) for the velocity modulus to lie between \( V \) and \( V + dV \) reads \[16\] :

\[
 W(V) = \frac{2V}{\pi} \int_0^{+\infty} dx \ f(x) \sin(xV) \]  

(1)

In our case, \( f(q, t, t_w) = f(x) \sim \exp[-(x\bar{V})^\mu] \) is proportional to the Fourier transform of the Levy stable law \[17\], \( L_{p,0}(V/\bar{V}) = \frac{1}{\pi} \int_0^{+\infty} dx \cos(xV) \exp[-(x\bar{V})^p] \). Thus, one obtains for the velocity distribution function :
\[ W(V) = -2V/\bar{V} \frac{d}{dV}[L_{p,0}(V/\bar{V})] \]

The Levy law is characterized by a broad tail: \( L_{p,0}(V/\bar{V}) \sim V^{-(p+1)} \) for \( V \gg \bar{V} \); Eq. 2 therefore predicts asymptotically \( W(V) \sim V^{-(p+1)} = V^{-(2.46 \pm 0.18)} \).

Simple arguments may account for this powerlaw dependence. The deformation field \( \Delta R(r, t) \) at a distance \( r \) from a source of stress is that of an elastic solid. In the absence of external stress sources, the leading (dipolar) term of a multipolar expansion of \( \Delta R \) is \( \alpha(t) r^{-2} \). Because of the relatively high elastic modulus of the material, the propagation of elastic stresses is almost instantaneous when compared to \( \tau_L \). Thus, the slow dynamics cannot be due to the propagation of the elastic deformation but rather to the time evolution of the strength of the internal stress sources. Therefore, the ballistic motion found by MDLS indicates \( \alpha(t) \sim t \) and \( V(r) = dR/dt \sim r^{-2} \). Note that a linear increase with time of the strain has been previously assumed in a phenomenological model for fractal gels \[11\] and is also obtained by a more sophisticated model \[15\]. For randomly distributed stress sources, the number of such sources at a distance between \( r \) and \( r + dr \) from any given point of the gel is \( dN \sim r^2 dr \). Therefore \( W(V) \sim dN/dV \sim r^5 \sim V^{-2.5} \), in very good agreement with the experimental results. Note that aging indicates that the internal stresses decrease with time, because either their strength \( \alpha \) or the number of sources \( N \) decreases.

The ballistic-motion rearrangement of the MLVs is also presumably responsible for the linear stress relaxation measured by rheology. The time scales measured by rheology and MDLS are however quite different. In fact, one might expect that a mechanical stress is relaxed when MLVs have moved over a distance \( l \) comparable to their size (\( l \approx 5 \mu m \)). The rheology relaxation time is then estimated to be of order of \( l/\bar{V} \). However, such value is more than three orders of magnitude larger than \( \tau_R \). This discrepancy underlines the fundamental difference between a DLS experiment and a rheology one. Although both probe the rearrangement of the MLVs, the two techniques are intrinsically measuring different quantities. In fact, \( \tau_L \) corresponds to the characteristic time for all scatterers to move over a distance \( 1/q \). By contrast, in rheology, rearrangements of a few MLVs may be sufficient to relax the applied stress; \( \tau_R \) is thus expected smaller than \( \tau_L \), as observed. In concentrated emulsions, it has indeed been measured that the motion of only a few percent of the particles is sufficient for the material to yield \[18\]. Moreover, the fact that the ratio \( \tau_R/\tau_L \) is constant suggests that the fraction of rearrangements required for yielding does not vary with sample age. Finally, we observe that although the stretching exponents \( m \) and \( p \) for rheology and MDLS are very different, they both reflect very broad distributions of times and velocities, respectively. To quantitatively relate the two distributions, more information about the fraction of rearrangements required for the material to yield would be needed.

The very peculiar time-dependent slow dynamics reported here should be observable with other repulsive systems, such as dense emulsions or foams, whose elasticity shares many features with that of MLVs gels. Moreover, the intriguing analogies found with colloidal gels \[11\], an attractive system, and with a micellar polycrystal \[19\] hint at a possible universality of such behavior in jammed soft materials. More experiments are needed to test this hypothesis.

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FIG. 1. Time and temperature dependency of the storage $G'$ (circles) and loss $G''$ (squares) moduli of a lamellar gel ($\Omega = 0.8$) (frequency 1 Hz, strain amplitude 1%); at $t = 1800$ sec the temperature is increased from 4.6 to 20°C (solid line). Age $t_w = 0$ of the gel is taken at the maximum of $G''$ (arrow). Inset: Optical microscopy picture showing the interface between the lamellar gel (left) and the solvent (right). Temperature is 20°C and scale bar is 20 µm.

FIG. 2. Relaxation modulus $G(t, t_w)$ following a step strain of amplitude 1% of a lamellar gel ($\Omega = 0.8$). For the sake of clarity, $G(t, t_w)$ has been normalized by its value $G_0$ at time $t - t_w = 0$. Curves are labeled by sample age $t_w$. 
FIG. 3. Scaling of $G/G_0$ versus $(t - t_w)/\tau_R$ for the data of Fig. 2. Inset: Age dependence of the relaxation time $\tau_R$ for a gel with $\Omega = 0.8$ (circles) and $\Omega = 1.2$ (squares). The straight line is a power law fit yielding an exponent of 0.78.

FIG. 4. Dynamic structure factors at $q = 11.2 \mu m^{-1}$ for a sample with $\Omega = 0.8$. Sample age is 7 min (squares), 1.5 h (circles), 5.6 h (crosses) and 14.3 h (stars). Solids lines are best fits using a stretched exponential function. Inset: Age dependence of $q\tau_L$, where $\tau_L$ is the characteristic time derived from MDLS and $q = 6.0$ (up triangles), 11.2 (down triangles) and 24.2 $\mu m^{-1}$ (diamonds). The straight line is a power law fit yielding an exponent of 0.77.
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