Intrinsic Aging and Effective Viscosity in the Slow Dynamics
of a Soft Glass with Tunable Elasticity

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We investigate by rheology and light scattering the influence of the elastic modulus, G_0, on the slow dynamics and the aging of a soft glass. We show that the slow dynamics and the aging can be entirely described by the evolution of an effective viscosity, η_{eff}, defined as the characteristic time measured in a stress relaxation experiment times G_0. At all times, η_{eff} is found to be independent of G_0, of elastic perturbations, and of the rate at which the sample is quenched in the glassy phase. We propose a simple model that links η_{eff} to the internal stress built up at the fluid-to-solid transition.

A large variety of disordered soft solids exhibit fast dynamics that are associated with overdamped elastic modes activated by thermal energy. As a consequence, the fast dynamics of systems such as polyelectrolyte or colloidal gels [1,2], concentrated emulsions [3], and surfactant or amphiphilic copolymer phases [4,5] is related to the elastic modulus, G_0, of the material. In addition, most of these systems exhibit a slow and nonstationary dynamics, whose origin is still under debate. One emerging idea is that the slow dynamics is due to the relaxation of internal stress built up at the fast transition from a fluid state to a solid state [5–9]. In this scenario, the internal stress would result from a deformation of the local structure with respect to the ideal, relaxed configuration and thus would be proportional to the elasticity of the system. Accordingly, one may expect the slow dynamics to be intimately connected to the elastic properties of the material. However, experiments that directly test these ideas are still lacking, due to the difficulty of quenching a system into a glassy phase without perturbing the internal stress distribution. Indeed, for most soft glasses the fluid-to-solid transition is obtained upon cessation of a large preshear [10–12], which certainly influences the initial configuration of internal stress [13].

In this Letter, we investigate the slow dynamics of a disordered soft material, for which G_0 can be varied over more than one decade without changing significantly the structure, and whose dynamics can be initialized without imposing any shear. The sample is formed by a compact arrangement of soft and polydisperse elastic spheres, where the transition from a fluid to a solid state can be controlled by varying the temperature. In a previous Letter [14] we have used multispeckle dynamic light scattering (MDLS) and linear rheology to show that this system exhibits slow dynamics, due to the rearrangement of the spheres, whose characteristic time increases as a power law of sample age, t_w. Here, we address explicitly the question of how the elasticity of the system influences the slow

dynamics. We show that τ_R, the characteristic time of the slow dynamics as measured in a stress relaxation experiment, depends only on the age of the sample and its elastic modulus. Remarkably, at all ages τ_R is found to be inversely proportional to G_0, thus suggesting that the slow dynamics and the aging of all samples can be described by the time evolution of a single parameter, an effective viscosity defined as $\eta_{\text{eff}} = \tau_R G_0$. Moreover, we show that the evolution of η_{eff} is independent of perturbations of the elastic modulus and of the rate at which the sample is quenched in the glassy phase. We propose a simple model that relates the age dependent effective viscosity to the relaxation of the internal stress.

The samples are surfactant lamellar phases constituted of a regular unidimensional stacking of bilayers that spontaneously roll up at temperature $T \gtrsim 10\,°C$, resulting in a dense packing of multilamellar vesicles (MLVs). The bilayers are composed of a mixture of a surfactant, cetylpyridinium chloride (CpCl), a cosurfactant, octanol (Oct) (weight ratio CpCl/Oct = 0.95), and an amphiphilic copolymer, Symperonics F68 by Serva $[(\text{EO})_{76} - (\text{PO})_{29} - (\text{EO})_{76}$, where EO is ethylene oxide and PO is propylene oxide]. The bilayers are diluted in brine ([NaCl] = $0.2M$) at a weight fraction ϕ, with $12\% \leq \phi \leq 16\%$ [15]. The F68/(CpCl + Oct) weight ratio α ranges between 0.2 and 1.6. The MLVs are polydisperse with a maximum size of a few microns [16]; due to their polydispersity and softness, their volume fraction is one. A temperature jump from $T = 4\,°C$ to $T \geq 10\,°C$ induces a fast transition from a fluid to a gel-like state and initializes the dynamics of the system [we take $t_w = 0$ as the time where $G'(1\text{ Hz}) \geq G''(1\text{ Hz})$, with G' (G'') the storage (loss) modulus measured by oscillatory rheology]. All measurements are performed at $T \geq 11\,°C$.

In the frequency range $5 \times 10^{-3} \leq \nu \leq 10$ Hz, the MLV phase behaves mechanically as a gel, G' being nearly ν independent and about 1 order of magnitude larger than G'' (see inset of Fig. 1). A simple model [16] relates the
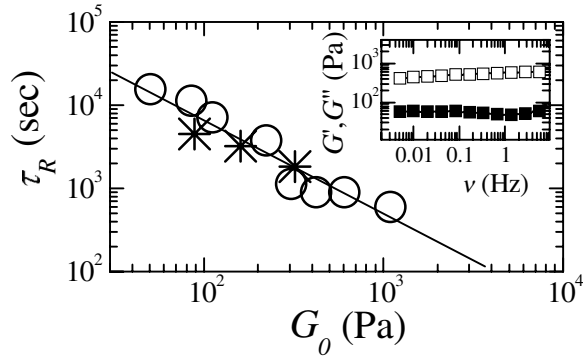
FIG. 1. Elastic modulus dependence of the characteristic time measured by linear rheology for samples with $\phi = 16\%$. $T = 20\,°C$ and $0.2 \leq \alpha \leq 1.6$ (○); $\alpha = 0.8$ and $T = 11$, 13.9, and 29.7 °C (*). The straight line is a fit to a power law yielding an exponent -1.1 ± 0.1. All measurements are done at the same age $t_w \simeq 24\,000$ s. Inset: storage (□) and loss (■) moduli measured in the linear regime, for a sample with $\phi = 16\%$, $\alpha = 1.2$, and $t_w = 61\,000$ s.

elastic modulus G_0 [experimentally, we take $G_0 \approx G'(1\,\text{Hz})$] to the MLV size distribution and the repulsive interaction between the bilayers. Both parameters depend on (i) the interlamellar distance, set by ϕ, (ii) the amount of copolymer adsorbed to the bilayer, α, and (iii) the hydrophobicity of the PO block of the copolymer, controlled by T. Thus, G_0 can be varied experimentally by changing three independent parameters, ϕ, α, and T.

On a time scale much larger than that accessed by oscillatory rheology, the dynamics is probed by measuring the stress relaxation, $\sigma(\tau)$, that follows a step strain imposed in the linear regime. For all samples, the stress relaxation is well described by $\sigma(\tau) = \sigma_0 \exp[-(\tau/\tau_R)^p]$ down to $\sigma \approx 0.1\sigma_0$, with p in the range 0.2–0.4, depending on sample composition [14]. Although measurements at even longer times are precluded by mechanical instability and aging, the data clearly indicate that most of the imposed deformation is eventually relaxed. Thus, at a very long time the MLVs behave essentially as a viscoelastic fluid, due to an ultraslow rearrangement dynamics. In Fig. 1 we show τ_R, extracted from the stretched exponential fit of $\sigma(\tau)$ [17], as a function of G_0 for samples with the same age ($t_w \simeq 24\,000$ s) and surfactant content ($\phi = 16\%$), but different G_0. The elastic modulus was varied either by changing copolymer content α at fixed T (circles) or by varying T at fixed α (stars). Strikingly, both sets of data collapse onto a master curve, for which τ_R monotonically decreases as G_0 increases, thus indicating that the slow dynamics is faster for harder systems, independent of the detailed sample composition. A power law fit to the data yields an exponent -1.1 ± 0.1, suggesting that the slow dynamics may be described by introducing an effective viscosity defined by $\eta_{\text{eff}} = \tau_R G_0$, whose value is independent of the composition and of the elasticity of the material over more than 1 order of magnitude in G_0.

To test the robustness of the concept of effective viscosity, we follow the aging of samples of various composition, and thus different elasticity (both ϕ and α were varied leading to $60 \leq G_0 \leq 700$ Pa). Each sample is quenched in the solid phase and aged without any perturbation during a time t_w before being submitted to a step strain allowing the measurement of τ_R, as described previously [18]. For all samples, we find that $\tau_R \sim t_w^m$ with an average exponent $\bar{m} = 0.87 \pm 0.09$, consistent with our previous experiments [14] and similar to that observed for other soft glassy materials [6,10,12]. Remarkably, all data collapse onto a single master curve when plotting the age dependence of the effective viscosity $\eta_{\text{eff}} = \tau_R G_0$, as shown in Fig. 2. This scaling demonstrates that not only does the effective viscosity characterize the slow dynamics at a given age, but it also accounts for the aging of samples with different elasticity in a unified way.

The aging behavior of many glassy systems is deeply affected by a temperature [19] or a mechanical [13,20] perturbation, leading to surprising effects such as the memory effect and rejuvenation. The question naturally arises whether the effective viscosity introduced here for the MLV phase is sensitive to a perturbation of the elastic modulus during the aging. To address this issue, we study the time evolution of the dynamics of a sample quenched from $T = 4$ to 26 °C and afterwards submitted to a square wave temperature perturbation, from 26 down to 20 and back to 26 °C, resulting in a variation of the elastic modulus of 20%. We follow the aging by MDLS at a scattering vector $q = 13.1\ \mu\text{m}^{-1}$, corresponding to a length scale $\simeq 0.5\ \mu\text{m}$, a significant fraction of the MLV size. The multispeckle technique allows time resolved information on the dynamics to be obtained, thus probing both the aging behavior and the instantaneous response of the soft glass configuration to the change in temperature. Figure 3(a) shows $g_2(t_w, t_w + t) - 1$, the two time intensity correlation function, measured before, during, and
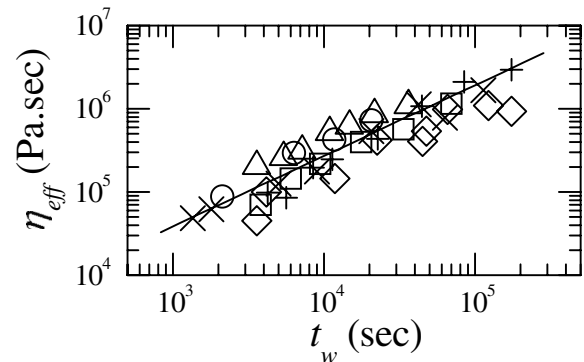

FIG. 2. Age dependence of the effective viscosity $\eta_{\text{eff}} = \tau_R G_0$ for samples at $T = 20\,°C$ and with the following values of ϕ and α, respectively: 12%, 0.8 (□); 16%, 0.3 (○); 16%, 0.4 (△); 16%, 0.8 (◇); 16%, 1.2 (×); 18%, 0.8 (+). The straight line is a power law fit to all the data yielding an exponent 0.85 ± 0.04.
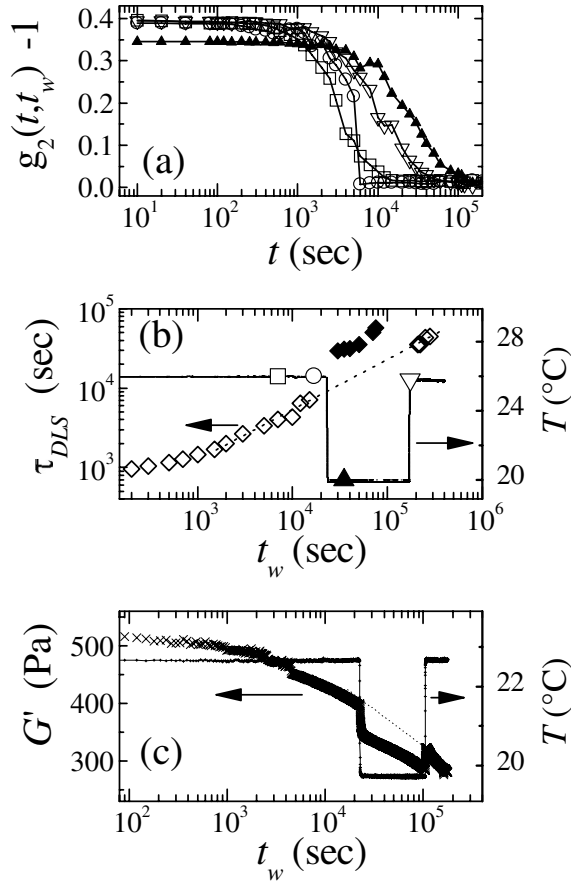
FIG. 3.   (a) Intensity correlation functions taken at age $t_w =$ 7000 s ($\square$), 17 000 s ($\bigcirc$), 35 000 s ($\blacktriangle$), and 175 000 s ($\triangledown$) for a sample (with $\phi = 16\%$ and $\alpha = 0.8$) submitted to the temperature history shown in (b). (b) (Left axis) Age dependence of the characteristic time extracted from the correlation functions. (Right axis) The solid line shows the temperature of the sample, and the symbols indicate the times at which the correlation functions shown in (a) are measured. (c) Age dependence of the storage modulus measured at frequency $\nu = 1$ Hz, for a sample submitted to the temperature history shown as a solid line. The dashed lines in (b) and (c) are a guide for the eye.

after the temperature perturbation. Simultaneous with the temperature jump, the correlation function drops abruptly to 0 [circles in Fig. 3(a)], thus revealing that the temperature perturbation not only modifies G_0, but also significantly affects the local configuration [21]. The characteristic time of the decay of $g_2 - 1$, τ_{DLS} [22], is plotted in Fig. 3(b) as a function of age, for the same sample as in 3(a). Before the perturbation, τ_{DLS} exhibits a power law growth with sample age, as observed in previous work [14]. When the sample is cooled at $T = 20\,°C$, τ_{DLS} suddenly increases by more than a factor of 2; however, note that the growth of τ_{DLS} follows a trend similar to that before the temperature jump. Surprisingly, when T is increased to its initial value, τ_{DLS} drops abruptly and recovers the power law evolution it would have had if the temperature was never changed. Similar results have

been obtained for a positive square wave temperature perturbation. Light scattering data thus indicate that, in spite of the significant change in the local configuration and in the relaxation time produced by the T jump, the evolution of the dynamics is not affected by the perturbation but rather follows an "intrinsic aging" behavior.

It is tempting to associate this intrinsic aging with a steady growth of η_{eff} similar to that reported in Fig. 2 for the undisturbed soft glasses. Unfortunately, time resolved stress relaxation experiments that would directly confirm a continuous increase of η_{eff} for the samples submitted to a temperature perturbation are not available. Instead, we note that if the evolution of the dynamics does not depend on the elastic history of the sample, as suggested by the MDLS experiments, the rate at which the sample is quenched from the fluid to the solid phase should not modify the aging. (A slow and continuous increase of T may be viewed, in fact, as a series of small T increments.) In Fig. 4 we compare the characteristic time measured by rheology for samples brought from 4 to 20 °C either rapidly ("fast quench," heating rate $r = 0.64\,°C/\min$) or slowly ("slow quench," $r = 0.03\,°C/\min$). If t_w is defined as the time elapsed after reaching the final temperature (main plot), a marked difference exists between the aging of samples quenched at different r, as observed for spin glasses [19]. By contrast, the data for both fast and slow quench rates collapse onto a single curve (inset) when defining the age as the time elapsed since the material is a solid (defined by $G' \gtrsim G''$), as expected if the effective viscosity does not depend on the elasticity of the sample or its elastic history, but only on the time spent in the glassy phase.

To further support the intrinsic aging scenario and to gain insight on the physical mechanism responsible for the growth of η_{eff}, we follow the time evolution of $G'(1$ Hz) for a sample submitted to a temperature perturbation similar to that of the MDLS experiments. At constant tempera-
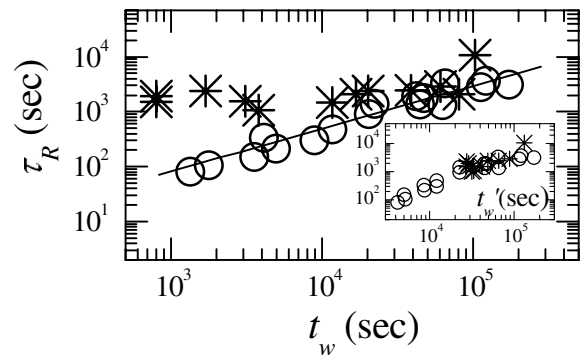

FIG. 4.   Characteristic relaxation time measured by rheology for a sample with $\phi = 16\%$ and $\alpha = 0.8$ that is brought from $T = 4$ to 20 °C rapidly ($\bigcirc$) or slowly (*). In the main plot the age t_w is defined as the time elapsed since T has reached its final value, while in the inset t'_w is defined as the time elapsed since the sample is solid.

ture, G' slowly but continuously decreases with time, as shown in Fig. 3(c). This behavior suggests that the storage modulus can be written as the sum of two contributions: the elastic modulus that would be reached at equilibrium, G_∞, and a term proportional to the internal stress, built up at the fast transition from the fluid to the solid phase and whose slow relaxation is responsible for the aging dynamics. When the temperature is varied from 23 to 20 °C, the storage modulus drops by 10%, a change in remarkable agreement with the difference of G' for samples directly quenched to these two temperatures. In analogy with the results of the MDLS experiments, when T is brought back to its initial value G' resumes the same time evolution it would have had without any temperature perturbation. These results provide additional evidence that the aging of the MLV phase is described by the evolution of an effective viscosity that depends only on t_w.

In order to rationalize our experimental findings, we present a simple model that links the effective viscosity to the internal stress, σ_{int}. In this picture σ_{int} stems from the elastic deformation of the MLVs with respect to a spherical shape, due to the random growth of closely packed MLVs at the fluid-to-solid transition. With time, the elastic deformation is slowly reduced through structural relaxations that are at the origin of the slow dynamics, leading to the aging behavior. We consider that the stress relaxation measured by rheology is due to rearrangements of regions of size L (presumably containing several MLVs) that are submitted to a driving force $\sim \sigma_{int} L^2$ and a viscous drag force $\sim \eta_{micro} L V$. Here, η_{micro} is a microscopic viscosity related to the solvent viscosity and the MLVs' volume fraction, and V is the local velocity of the rearranging zone. Balancing the driving force and the viscous drag yields $\sigma_{int} \sim \eta_{micro} V / L$. Because both the elastic modulus and σ_{int} have as a common microscopic origin the elastic energy due to the deformation of the MLVs, one expects σ_{int} to be, at all times, proportional to G_∞: $\sigma_{int}(t_w) = G_\infty / \xi(t_w)$, with $\xi(t_w)$ a dimensionless proportionality factor whose growth with t_w describes the relaxation of σ_{int} and thus the aging. As suggested previously, writing $G_0 = G_\infty + b\sigma_{int}$ (with b a proportionality factor), one gets $\sigma_{int} = G_0 / b(1 + \xi) \sim \eta_{micro} V / L$. Experimentally, the characteristic time of the stress relaxation is related to the time needed for a region of size L to move over a distance equal to its size, $\tau_R \sim L / V$. From $\eta_{eff} = G_0 \tau_R$, one finally obtains $\eta_{eff}(t_w) \sim \eta_{micro}[1 + \xi(t_w)]$. In agreement with experiments, this scaling shows that the effective viscosity is independent of the elastic modulus of the material and that the relaxation of the internal stress leads to an increase of η_{eff} with sample age. The intrinsic aging reported above suggests that neither an isolated temperature jump (Fig. 3) nor a series of very small T

increments (Fig. 4) is able to relax significantly the MLVs' deformation, although they change the local configuration, as indicated by the drop of $g_2 - 1$. As a consequence, they leave essentially unchanged ξ and hence η_{eff}. Increasing the amplitude or the number of T jumps may eventually suppress the intrinsic aging: experiments are in progress to test this conjecture. Finally, we note that the elasticity of the MLV phase is formally identical to that of concentrated emulsions [16]: our findings should therefore be directly generalizable to the latter. Whether the same conclusions may be drawn also for other concentrated soft systems, e.g., deformable colloidal particles, remains an open issue.

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