Interplay between Shear Loading and Structural Aging in a Physical Gelatin Gel

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We show that the aging of the mechanical relaxation of a gelatin gel exhibits the same scaling phenomenology as polymer and colloidal glasses. In addition, gelatin is known to exhibit logarithmic structural aging (stiffening). We find that stress accelerates this process. However, this effect is definitely irreducible to a mere age shift with respect to natural aging. We suggest that it is interpretable in terms of elastically aided elementary (coil → helix) local events whose dynamics gradually slows down as aging increases geometric frustration.

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Since glassy materials are out-of-equilibrium metastable systems, their physical properties slowly evolve with time, a process known as structural recovery, which gives rise to gradual aging of thermodynamic quantities. For instance, the specific volume of glassy polystyrene decreases logarithmically with age, i.e., waiting time t_w after quenching [1]. Besides, the rheological response to shear loading at age t_w depends on both the measurement time $t_w + t$ and t_w itself [2]. Creep compliances obey a self-similar scaling $J(t_w, t) = \mathcal{J}(t/t_w^{\mu})$. In polymer glasses, at low stress levels, the aging exponent $\mu \lesssim 1$. It decreases at large stresses approaching yield level. Whether such "rejuvenation" is truly equivalent to a shift of the age t_w still remains a matter of debate [1,3,4]. If such is not the case, as hinted by the work of McKenna on polymer glasses [1] and Viasnoff *et al.* [5,6] on a colloidal glass, a double question remains: (i) How can this process be understood in terms of exploration of configurational space? (ii) To what extent is the nature of the aging mechanism generic or dependent on the class of materials? In particular, is it associated with a growing length scale or not? Here we address this question on a jammed system of a different class, a gelatin gel, which, as we show, shares with glassy materials a common aging phenomenology. Beyond this, we analyze the subtle interplay between shear loading and structural aging with the help of original "assisted creep" experiments which enable us to conclude that in such network-based jammed systems aging is controlled by the slowing down dynamics of *local* relaxation events.

Gelatin is a physical gel; namely, its gelation is thermoreversible [7]. The sol state ($T > T_{\rm gel}$) is a solution of single chains of denatured collagen in water. Below $T_{\rm gel}$, renaturation of the native triple helix structure, stabilized by H bonds, becomes thermodynamically favorable, and chains form a percolating network of helical segments—the cross-links (CLs)—connected by single strand coils. Renaturation is frustrated by strong topological constraints: Indeed, since chains are very long (~μm), each of them is involved in many CLs, hence a large interchain connectivity. As time t_w after quench increases, after a rapid initial rise, the gel stiffness $\mathcal{G}(t_w)$ reaches a slow, logarithmic growth regime (Fig. 1), the termination of which has never been observed [8]. Several studies [9,10] converge towards a common picture: While, at early times, structural aging results mainly from the increase of the number of CLs, in the log regime it is essentially controlled by CL growth and internal rearrangements. Because of the large interconnectivity, CL growth induces growing internal tensions and torques on the network-forming coil strands. This is what we call "increasing geometric frustration." The mechanical relaxation spectrum consists of two well separated parts [7]: (i) a high-frequency band (typically $\omega > 10^5$ rad · s^{-1}) due to the viscoelasticity of coil segments (of length the mesh size ξ typically ~10 nm) and (ii) an ultralow frequency one, which gives rise to slow creep [11] and stress relaxation [12]. At intermediate frequencies, the gel is purely elastic and characterized by its small-strain shear modulus.

In summary, as already proposed by Normand and Parker [13], gelatin exhibits glasslike aging. Here we investigate in detail the age dependence of mechanical relaxations and the interplay between structural aging, as

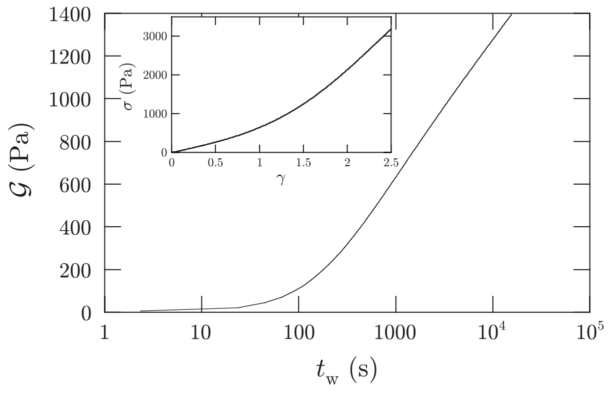

FIG. 1. Aging of the small-strain shear modulus $\mathcal{G}$ measured at 10 Hz and strain amplitude 10^{-3} at temperature $T = 20\,^{\circ}$C. Inset: Loading curve at age $t_w = 1000$ s.

measured via the evolution of the shear modulus, and external loading.

Experimental.—Samples are prepared by dissolving 5 wt % gelatin (300 Bloom, from porcine skin, Sigma) in deionized water at 80 °C. The gelation temperature is $T_{\mathrm{gel}} \simeq 29\,^\circ\mathrm{C}$. The pregel solution is poured into the sandblasted cone-plate cell of a stress-controlled rheometer (Anton Paar, MCR 501), protected against solvent evaporation by a dodecane rim. The sample temperature is first set at $T_0 = 50\,^\circ\mathrm{C}$ and then ramped at 7.5 °C/ min down to the working temperature T. Unless otherwise specified, $T = 20 \pm 0.1\,^\circ\mathrm{C}$. We define the onset of gelation, taken to be the origin of waiting times t_w, as the time where the loss tangent $\tan\delta = 1$. Reinitialization of the gel history is performed by reheating up to T_0, shearing at $\dot{\gamma} = 1\ \mathrm{s}^{-1}$ for 200 s, and then repeating the quench. We have checked that this protocol ensures that $\mathcal{G}(t_w)$, as well as relaxation curves, are reproducible to within 1%, over 20 cycles at least. Thanks to this, we are able to probe the structural evolution along the course of a relaxation in a fully nonperturbative way. For example, when probing stress relaxation of a gel of age t_w, we let it relax for a time t and then measure the small-strain modulus $G(t, t_w)$ immediately after fast unloading at time $t_w + t$. The sample is then reinitialized, and the process is repeated with a different t value.

The stiffness of the gel is controlled, over a wide strain range, by the entropic elasticity of single strand coils. A typical loading curve $\sigma(\gamma)$ is shown in Fig. 1 (inset). The linear range extends up to $\gamma \approx 40\%$, beyond which the gel strain hardens. At $\gamma \approx 350\%$, apparent failure is observed, resulting from wall slip. So we cannot reach shear melting (known from fracture studies [14] to occur for stresses $\sim 10^2\mathcal{G}$) nor failure of the material itself, and our experiments pertain to the strongly subyield regime.

The evolution with waiting time of the stress relaxation (SR) and creep (Cr) responses is shown in Figs. 2(a) and 2(c), which correspond to loadings in the linear elastic range. In this regime, we find that the responses are themselves linear, characterized by the creep compliance $J(t_w, t)$ and the stress relaxation modulus $Y(t_w, t)$.

Figures 2(b) and 2(d) show that both quantities can be quite satisfactorily collapsed by rescaling time by t_w-dependent factors θ_Y and θ_J, which we find (see insets) to obey, over more than 2 decades, power law scalings with the same exponent:

$$\theta_{Y,J} \sim t_w^{\mu}, \quad \text{with} \quad \mu = 1.25 \pm 0.02. \tag{1}$$

So, in the strongly subyield regime, gelatin exhibits the same scaling phenomenology as glasses. Yet, while most glassy materials are of the subaging type ($\mu < 1$) [1,4], gelatin turns out to be hyperaging.

Closer inspection of Fig. 2(b) reveals a noticeable splay of the scaled curves beyond $t/\theta_Y \approx 1$ (also present in Fig. 4 of [15]). Moreover, a trend towards saturation of the shear stress at a finite level is clearly visible [see also Fig. 2(a)]. Creep curves for young gels ($t_w \leq 100$ s) exhibit, after a quasilogarithmic intermediate regime, a similar trend towards strain saturation. How can we understand this previously unreported behavior? It is natural here to decompose the total strain γ as the sum of an elastic component and a plastic one, i.e.,

$$\gamma = \frac{\sigma}{G} + \gamma_{\mathrm{pl}}, \quad \text{with} \quad \sigma\dot{\gamma}_{\mathrm{pl}} \geq 0. \tag{2}$$

It is then clear that the results of standard relaxation experiments at constant σ or γ mix information about the aging of structure and of flow properties. Indeed, although its dynamics may be affected by the mechanical perturbation, structural aging is certainly at work, so that, for large $t \gg t_w$, the value of G is certainly not coded simply by the initial age t_w but, rather, by the true one ($t_w + t$). Hence we have the limited validity of the above scaling and the need

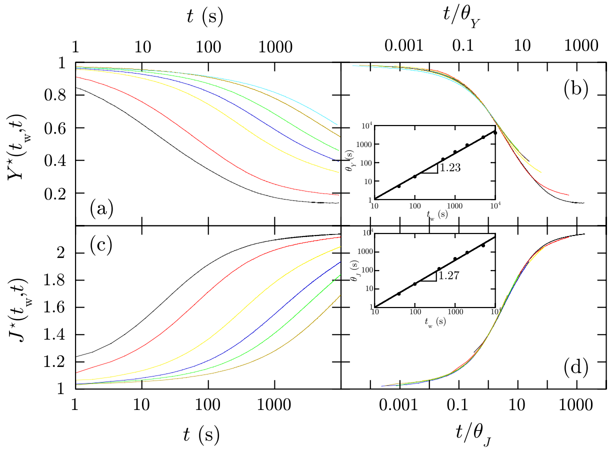

FIG. 2 (color online). (a) Normalized stress relaxation modulus $Y^\star(t_w, t) = Y(t_w, t)/Y(t_w, 0)$ for waiting times, from bottom to top, $t_w = 40$, 100, 500, 10^3, 2×10^3, 5×10^3, and 10^4 s. (b) The same data as (a) plotted vs rescaled time $t/\theta_Y(t_w)$. $\theta_Y(t_w)$ (see inset) is chosen so that $Y^\star(t_w, \theta_Y) = 0.7$. (c) Normalized creep compliance $J^\star(t_w, t) = J(t_w, t)/J(t_w, 0)$ for waiting times, from top to bottom, $t_w = 40$, 100, 400, 10^3, 2×10^3, and 5×10^3 s. (d) The same data as (c) plotted vs rescaled time $t/\theta_J(t_w)$. $\theta_J(t_w)$ (see inset) is chosen so that $J^\star(t_w, \theta_J) = 1.4$.

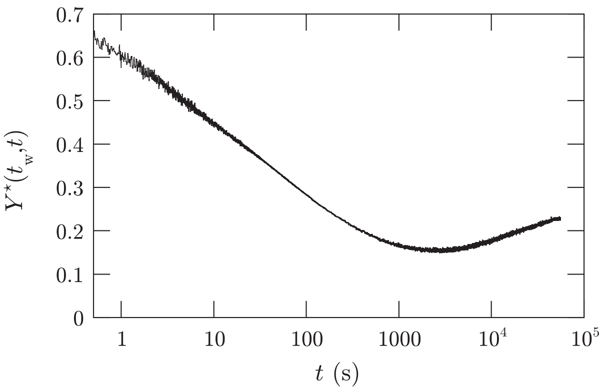

FIG. 3. Normalized stress relaxation modulus vs time for a gel of age $t_w \simeq 10$ s at temperature $T = 10\,^\circ\mathrm{C}$.

for characterizing structural aging under mechanical perturbations.

We systematically measured the elastic modulus $G(t_w, t)$ along the course of SR experiments performed at various t_w and γ levels in the linear elastic regime. We find that, within experimental accuracy, in all cases $G(t_w, t) = \mathcal{G}(t_w + t)$; i.e., under such conditions, natural structural aging is unperturbed and is likely to control the long-term dynamics. If so, $\dot{\sigma} = \dot{\mathcal{G}}\sigma/\mathcal{G} - \dot{\gamma}_{\mathrm{pl}}\mathcal{G}$ might change sign. We have indeed evidenced such a late ($t \gtrsim 300 t_w$) stress buildup regime (see Fig. 3) by taking advantage of the fact that cooling from 20 to 10 °C increases the natural aging log rate by a factor of 2.5 [7]. This behavior is the SR analog of the reversal between early creep and late strain recovery observed and interpreted by Cloitre *et al.* (see [15], Fig. 4).

SR is certainly poorly suited to reveal a possible shear sensitivity of structural aging since, even for large imposed strains, σ remains noticeable only for a limited time. We have therefore measured $G(t_w, t)$ in the Cr configuration. Again, no departure from natural aging is measurable, for t values up to $500 t_w$, up to stress levels $\sigma = \mathcal{G}(t_w)$ corresponding to *initial* strains of 100%. However, since the network gradually stiffens, the dimensionless strength $\sigma/\mathcal{G}$ decreases, and stress itself is probably not a good control parameter. To circumvent this drawback, we have devised "assisted creep" (ACr) experiments in which we apply to the sample an increasing stress $\sigma = \gamma_0 \mathcal{G}(t_w + t)$, with $\mathcal{G}$ the value for natural aging. This protocol is meant to work, as far as possible (see the caption of Fig. 4), at constant elastic strain $\gamma_{\mathrm{el}} = \gamma_0$.

Figure 4 shows the results of a standard and an assisted creep experiment performed on equally aged gels. The ACr enhancement of the flow dynamics $\gamma_{\mathrm{pl}}(t)$ [Eq. (2)] in the intermediate, quasilogarithmic regime is spectacular. We have performed a set of ACr runs in which various values of γ_0 are applied to a gel of age $t_w = 400$ s for a duration $\Delta t = 700$ s after which we unload to zero shear stress. The small-strain modulus, measured during and after the mechanical perturbation, is shown in Fig. 5(a). The effect of external loading is now unmistakable: (i) Under a finite γ_0, structural aging is accelerated. The larger γ_0, the larger the log slope $\beta = \partial G/\partial(\log t)$ [see Fig. 5(b)]; (ii) after unloading, β recovers its $\sigma = 0$ value ($\beta_0 = 700$ Pa) and, for $t > t_w + \Delta t$, the only memory of the loading episode kept by the system consists in a rigid shift of G with respect to its "natural" value $\mathcal{G}(t_w + t)$. So, although loading induces accelerated structural strengthening, this effect is by no means equivalent to a mere forward shift of the "natural age." We thus confirm the conclusion of Refs. [1,5] that mechanical perturbations of slow glasslike relaxation cannot truly be termed overaging (nor, alternately, rejuvenation).

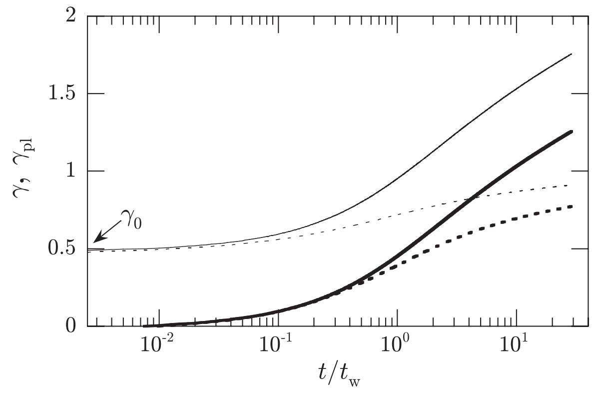

FIG. 4. Assisted (full curves) and standard (dashed curves) creep total (thin lines) and plastic (thick lines) strain responses for a gel of age $t_w = 400$ s and for $\gamma_0 = 0.5$. At the end of the ACr run, $\gamma_{\mathrm{el}} = 0.97\gamma_0$.

Discussion.—One step further, the above set of results leads us to propose the following tentative picture for physical aging in gelatin. As proved by Djabourov *et al.* [16], G and the helix fraction obey a one-to-one relation. We focus here on the logarithmic regime where nucleation of new CLs is negligible, so that natural aging is ruled by the growth of preexisting ones [10], at the expense of the connecting coils, the stiffness of which controls the gel

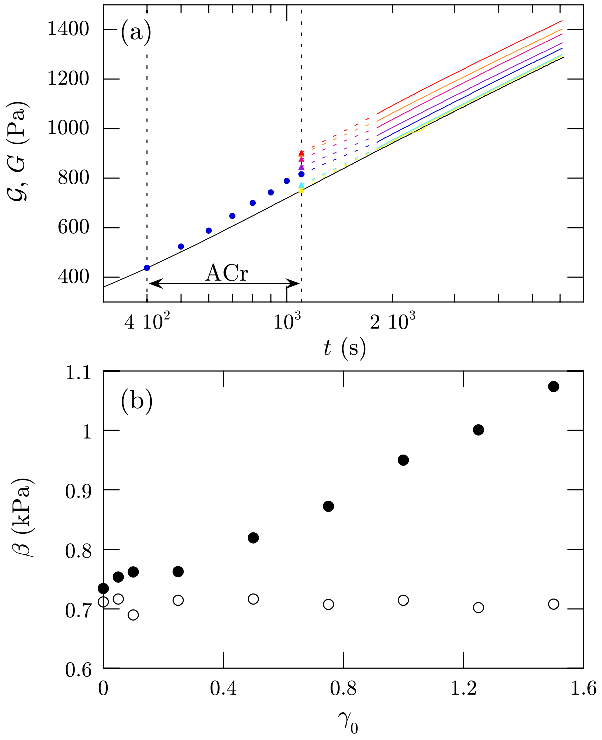

FIG. 5 (color online). (a) Dots: Aging of the shear modulus G during an ACr experiment with $\gamma_0 = 0.5$. Each datum is obtained from the unloading slope of a run stopped at t (see text). Lines: Aging after strain recovery following an ACr under γ_0 values, from bottom to top, $\gamma_0 = 0.05$, 0.1, 0.25, 0.5, 0.75, 1.0, 1.25, and 1.5. Triangles show unloading slopes at the end of the ACr phase. Thick line: Natural aging $\mathcal{G}(t)$. (b) Aging log slope β during (full dots) and after (empty dots) assisted creep plotted v. γ_0.

modulus. So, due to solvent incompressibility, the average mesh size remains quasiconstant and G grows. The formation of a new unit helix segment (h) can be pictured as a H-bonding reaction involving one monomer from each of the three coils (c) emanating from the CL end. In order for the reaction ($c \longrightarrow h$) to proceed, these three monomers must ''meet'' in the proper positional and orientational configuration. This topological constraint can be depicted as an entropic activation barrier separating the c state from the energetically favorable h one ($F_h < F_c$).

As shown by Kutter and Terentjev [17], as the coil length decreases under these conditions, F_c itself decreases. At the same time, coil shortening induces a thinning of the entropy supply and thus an increase of the barrier height F_b. In the spirit of the analysis by Knoll *et al.* [18] of the relaxation kinetics of nanoindents in a polymer glass, we make the schematic assumption that (i) the barrier height $\mathcal{E} = F_b - F_c$ increases linearly with the average helix fraction χ (i.e., with CL length), and (ii) χ evolves with an Arrhenius dynamics $\dot{\chi} = \tau^{-1} \exp[-\epsilon\chi/k_B T]$, with $\epsilon = d\mathcal{E}/d\chi$ the ''sensitivity to frustration.'' This highly schematic model predicts that the frustration-induced slowing down of the $c \longrightarrow h$ reaction results in a logarithmic dynamics where the slope $d\chi/d\ln t = k_B T/\epsilon$ is controlled by the sensitivity parameter ϵ.

When an elastic strain γ_{el} is imposed, the elastic energy is stored in the compliant coil, leading to an upward shift ΔF_c and thus to acceleration of aging. The barrier free energy is also shifted, though in an anisotropic fashion: Along the stretching (respectively, compressive) principal direction, coil entropic wandering is restricted (respectively, facilitated) and $\Delta F_b > 0$ (respectively, <0). So CLs grow faster along the compressed direction than along the stretched one. When unloading, the corresponding relative coil shortening leads to a remanent, plastic strain. We believe creep to be due to this texturing [19], differential rate-of-growth effect, rather than to CLs ''melting'' under stress, as initially proposed by Ferry. Indeed, on the one hand, the probability of the $h \longrightarrow c$ reaction is negligibly small with respect to that of the $c \longrightarrow h$ one, since the binding energy $F_c - F_h$ is on the order of that of 3 H bonds (~ 0.3 eV $\gg k_B T$) [20]. On the other hand, melting would be contradictory with the observed stress-induced acceleration of stiffening. Finally, once the ''mechanically overaged'' system is unloaded, the elastic shift is suppressed, and the CL growth dynamics returns to the natural one, the memory of the perturbation being encoded in the height reached by the entropic barrier at the end of the loading phase. Hence we have the recovery of the log slope β.

In summary, the experimental results of a coupled study of mechanical relaxations and of the stress-induced acceleration of the stiffening dynamics lead us to propose that physical aging in gelatin gels can be described in terms of *local* irreversible events. Namely, we picture CL growth as the sequential formation of unit helix segments, via activation over an entropic barrier whose height increases with the degree of completion of relaxation towards thermodynamic equilibrium. That is, this barrier height appears, roughly speaking, as an ''order parameter'' into which geometric frustration effects are lumped. Whether such a local scenario for aging would also hold in glassy systems remains a fully open issue. If so, it would mean that aging would be controlled by the growth of the instability threshold of the cage (cluster) rearrangements and hence by the relaxation of the average free volume. This is precisely the subject of an active ongoing debate. We believe that experimental studies such as that of specific volume relaxation *after* an ''implosion'' episode of the type reported by McKenna could bring valuable insight into this issue.

[1] G. B. McKenna, J. Phys. Condens. Matter **15**, S737 (2003).
[2] L. C. E. Struik *Physical Aging in Polymers and Other Amorphous Materials* (Elsevier, Amsterdam 1978).
[3] J. Röttler and M. Warren, Eur. Phys. J. Special Topics **161**, 55 (2008).
[4] M. Warren and J. Röttler, Phys. Rev. E **78**, 041502 (2008), and references therein.
[5] V. Viasnoff and F. Lequeux, Phys. Rev. Lett. **89**, 065701 (2002).
[6] V. Viasnoff, S. Jurine, and F. Lequeux, Faraday Discuss. **123**, 253 (2003).
[7] K. te Nijenhuis, Adv. Polym. Sci. **130**, 160 (1997).
[8] V. Normand, S. Muller, J.-C. Ravey, and A. Parker, Macromolecules **33**, 1063 (2000).
[9] J. L. Gornall and E. M. Terentjev, Phys. Rev. E **77**, 031908 (2008).
[10] L. Guo, R. H. Colby, C. P. Lusigan, and A. M. Howe, Macromolecules **36**, 10 009 (2003).
[11] P. M. Gilsenan and S. B. Ross-Murphy, Int. J. Biol. Macromol. **29**, 53 (2001).
[12] M. Miller, J. D. Ferry, F. W. Schremp, and J. E. Eldridge, J. Phys. Chem. **55**, 1387 (1951).
[13] V. Normand and A. Parker, in *Proceedings of the 3rd International Symposium on Food Rheology and Structure* (ETH Zürich, Zürich, 2003), p. 185.
[14] T. Baumberger, C. Caroli, and D. Martina, Nature Mater. **5**, 552 (2006).
[15] M. Cloitre, R. Borrega, and L. Leibler, Phys. Rev. Lett. **85**, 4819 (2000).
[16] C. Joly-Duhamel, D. Hellio, A. Ajdari, and M. Djabourov, Langmuir **18**, 7158 (2002).
[17] S. Kutter and E. M. Terentjev, Eur. Phys. J. E **8**, 539 (2002).
[18] A. Knoll, D. Wiesmann, B. Gotsmann, and U. Duerig, Phys. Rev. Lett. **102**, 117801 (2009).
[19] An analogous shear-induced texturing effect in silica glass is reported in C. L. Rountree, D. Vandembroucq, M. Talamali, E. Bouchaud, and S. Roux, Phys. Rev. Lett. **102**, 195501 (2009).
[20] T. Baumberger and O. Ronsin, J. Chem. Phys. **130**, 061102 (2009).