Interplay between shear loading and structural aging in a physical gel

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Abstract

We show that the aging of the mechanical relaxation of a gelatin gel exhibits the same scaling phenomenology as polymer and colloidal glasses. Besides, 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 $J(t_w, t) = J(t/t_w^\mu)$. 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 works of McKenna on polymer glasses [1] and Viasnoff et al. [3, 5] on a colloidal glass, a double question remains: (i) how can this process be understood in terms of exploration of configurational space? (ii) to which extent is the answer generic or dependent on the class of materials?

In order to shed further light on these questions, we report here the results of a study of aging in a gelatin gel. Gelatin is a physical gel, namely its gelation is thermoreversible [7]. The sol state ($T > T_{gel}$) is a solution of single chains of denatured collagen in water. Below $T_{gel}$ 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 (CL) — connected by single strand coils. Renaturation is frustrated by strong topological constraints: indeed, since chain length is very long ($\sim \mu$m), each of them is involved in many CL, hence a large interchain connectivity. As time after quench increases, after a rapid initial rise, the gel stiffness 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 CL, in the log regime it is essentially controlled by CL growth and internal rearrangements. Due to 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 [11]: (i) a high-frequency band, (typically $\omega > 10^5$ rad.s$^{-1}$) due to the viscoelasticity of coil segments (of length the mesh size $\xi$ typically $\sim 10$ nm) (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 $G$. 

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In summary, as already shown by Normand [13], gelatin exhibits a behavior akin to glassy
dynamics. Here we investigate in detail the age dependence of mechanical relaxations and
the interplay between structural aging, as measured via the evolution of $G$, and external
loading.

![Graph showing the aging of the small strain shear modulus $G$ measured at 10 Hz and strain amplitude $10^{-3}$ at temperature $T = 20^\circ C$. Insert: loading curve at age $t_w = 1000$ s.]

**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 $T_{gel} \approx 29^\circ C$.
The pregel solution is poured into the sand-blasted cone-plate cell of a stress-controlled
rheometer (Anton Paar, MCR 501), protected against solvent evaporation by a dodecane
rim. Mechanical stability of the whole rheometer has been improved by enclosing it into a
box, thermalized at 20±0.1°C. Sample temperature is first set at $T_0 = 50^\circ C$, then ramped at
7.5°C/min down to the working temperature $T$. Unless otherwise specified, $T = 20\pm 0.1^\circ C$.

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 $\dot{\gamma} = 1$ s$^{-1}$ for 200 s, then repeating the quench. We have checked that this
protocol ensures that $G$, as well as relaxation curves, are reproducible to within 1%, over 20
cycles at least. Thanks to this, we are able to probe the evolution of $G$ along the course of
a relaxation in a fully non-perturbative way. For example, when probing stress relaxation
of a gel of age $t_w$, we let it relax for a time $t$, then measure $G(t, t_w)$ immediately after fast
unloading. 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

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of single strand coils. A typical loading curve $\sigma(\gamma)$ is shown on Fig.1 (inset). The linear range extends up to $\gamma \approx 40\%$, beyond which the gel strain-hardens. At $\gamma \approx 250\%$, apparent failure is observed, resulting from wall slip. So, we cannot reach shear melting (known from fracture studies \[14\] to occur for stresses $\sim 10^2 G$), nor failure of the material itself, and our experiments pertain to the strongly sub-yield regime.

The evolution with waiting time of the stress relaxation (SR) and creep (Cr) responses is shown on Figs.2.a,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 $Y(t_w, t)$.

![Graphs showing stress relaxation and creep responses](image)

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

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

$$\theta_Y, J \sim t_w^\mu \text{ with } \mu = 1.25 \pm 0.02$$ (1)

So, in the strongly sub-yield regime, the gel system exhibits the same rheological aging phenomenology as glasses. Yet, while most glassy materials are of the sub-aging type ($\mu < 1$)
gelatin turns out to be hyper-aging. However, closer inspection of Fig.2.b reveals a noticeable splay of the scaled curves beyond $t/\theta_Y \approx 1$. 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 quasi-logarithmic 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 $\gamma$ as the sum of an elastic component and a plastic one, i.e.:

$$\gamma = \frac{\sigma}{G} + \gamma_{pl} \quad (2)$$

It is then clear that the results of standard relaxation experiments at constant $\sigma$ or $\gamma$ 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 the limited validity of the above scaling and the need for characterizing structural aging under mechanical perturbations.

We systematically measured the elastic modulus $\tilde{G}(t_w, t)$ along the course of SR experiments performed at various $t_w$ and $\gamma$-levels in the linear elastic regime. We find that, within experimental accuracy, in all cases $\tilde{G}(t_w, t) = G(t_w + t)$, i.e. under such conditions, natural structural aging is unperturbed, and is likely to control the long term dynamics. If so, $\dot{\sigma} = \dot{G}\sigma/G - \dot{\gamma}_{pl}G$ might change sign. We have indeed evidenced such a late ($t \gtrsim 300 t_w$) stress build-up 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]. We suggest that this behavior might be the SR-analog of the reversal between early creep and late strain recovery observed by Cloitre et al. (see [15], figure 4).

SR is certainly poorly suited to reveal a possible shear-sensitivity of structural aging since, even for large imposed strains, $\sigma$ only remains noticeable for a limited time. We have therefore measured $\tilde{G}(t_w, t)$ in the Cr configuration. Again, no departure from natural aging is measurable, for $t$ values up to 500$t_w$, up to stress levels $\sigma = G(t_w)$ corresponding to initial strains of 100%. However, since the network gradually stiffens, the dimensionless strength $\sigma/\tilde{G}$ decreases, and stress itself is probably not a good control parameter. As an attempt to circumvent this drawback, we have devised “assisted creep” (ACr) experiments in which we apply to the sample an increasing stress $\sigma = \gamma_0 G(t_w + t)$ with $G$ the value for natural
FIG. 3: Normalized stress relaxation modulus vs. time for a gel of age $t_w \simeq 10$ s at temperature $T = 10^\circ$ C.

aging. This protocol is meant to work, as far as possible, at constant elastic strain $\gamma_{el} = \gamma_0$.

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. At the end of the ACr run, $\gamma_{el} = 0.97\gamma_0$.

Fig.4 shows the results of a standard and an assisted creep experiments performed on equally-aged gels. The ACr enhancement of the flow dynamics $\gamma_{pl}(t)$ (eq. (2)) in the intermediate, quasi-logarithmic regime is spectacular. We have performed a set of ACr runs in which various values of $\gamma_0$ 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 on Fig.5. The effect of external loading is now unmistakable: (i) under a finite $\gamma_0$, structural aging is accelerated. The larger $\gamma_0$, the larger the log-slope $\tilde{\beta} = d\tilde{G}/d(\log t)$ (see inset) (ii) after unloading, $\tilde{\beta}$ recovers its $\sigma = 0$ value ($\beta = 700$ 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 $\tilde{G}(t)$ with respect to its “natural” value $G(t)$. 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 McKenna and Viasnoff et al. that mechanical perturbations of slow glass-like relaxation cannot truly be termed overaging (nor, alternately, rejuvenation).

![Graph](image)

**FIG. 5:** (a) Dots: aging of the shear modulus $\tilde{G}(t)$ during an ACr experiment with $\gamma_0 = 0.5$. Each datum is obtained by the unloading slope of a run stopped at $t$ (see text). Lines: aging after strain recovery following an ACr under $\gamma_0$ 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 $G(t)$. (b) Aging log-slope $\tilde{\beta}$ during (full dots) and after (empty dots) assisted creep plotted vs. $\gamma_0$.

**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 CL 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 modulus $G$. So, due to solvent incompressibility, the average mesh size remains quasi-constant 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 → 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 nano-indents in a polymer glass, we make the schematic assumption that (i) the barrier height \( E = F_b - F_c \) increases linearly with the average helix fraction \( \chi \) (i.e. with CL length) (ii) \( \chi \) evolves with an Arrhenius dynamics \( \dot{\chi} = \tau^{-1} \exp[-\epsilon \chi/k_B T] \) with \( \epsilon = dE/d\chi \) the “sensitivity to frustration”. This highly schematic model predicts that the frustration-induced slowing down of the c→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 \( \epsilon \).

When an elastic strain \( \gamma_{el} \) is imposed, the elastic energy is stored in the compliant coil, leading to an upward shift \( \Delta F_c \) and thus to acceleration of aging. The barrier free energy is also shifted, though in an anisotropic fashion: along the stretching (resp. compressive) principal direction, coil entropic wandering are restricted (resp. facilitated) and \( \Delta F_b > 0 \) (resp. < 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, differential rate-of-growth effect, rather than to CL “melting” under stress, as initially proposed by Ferry. Indeed, on the one hand, the probability of the h→c reaction is negligibly small with respect to that of the c→h one, since the binding energy \( F_c - F_h \) is on the order of that of 3 H-bonds (\( \sim 0.3 \text{ eV} \gg k_B T \)) [19]. 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 the recovery of the log-slope \( \beta \).

In summary, the experimental results of a coupled study of mechanical relaxations and of the stress-induced acceleration of the stiffening dynamics leads 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 simple, local description of aging could make sense in glassy systems remains an open issue. If so, it would mean that aging would be controlled by the growth of the instability threshold of the local cluster rearrangements, 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.

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