

How do Self-Assembling Polymers and Gels Age Compared to Glasses?

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Experiments on gels have provided contradictory results concerning the relation between correlation and response functions during aging. To clarify this puzzle, we numerically investigate the fluctuation-dissipation plot in equilibrium polymers and in network forming gels employing two distinct observables, (i) the density Fourier transform and (ii) the single-particle potential energy, to probe (i) diffusional processes and (ii) the development of a bond network. The plot behaves very differently for the two cases. Violation from the equilibrium behavior is found only for the second observable. The experimental implications of the discovered sensitivity to the choice of the probe are discussed, in particular, with respect to the existing experimental results.

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Introduction.—Gels are important materials present in countless technological applications (foods, cosmetics, biomedical devices, thermal insulators, etc.). From a more fundamental-physics point of view, gels are examples of arrested states of matter, members of the remarkable class of systems which display glassy dynamics. Glassy systems have attracted considerable interest as nonequilibrium systems since, albeit very different from each other, they all share common properties. Correlation functions decay as power laws or stretched exponentials, usually with distinctive “fast” and “slow” relaxation mechanisms. Moreover, structural and dynamic properties depend on the time elapsed since the system was driven out of equilibrium, a phenomenon called “aging” [1,2]. In glassy systems, the response to an external perturbation is connected to the decay of the spontaneous fluctuations differently than in equilibrium. Theory suggests that the relation between response and perturbation falls in three distinct universal classes, namely, coarsening, two-time-scales, and many-time-scales classes [3,4].

Studies of the fluctuation-dissipation theorem (FDT) violations [5] have concentrated on high-density glass forming liquids [6–12], finding a linear relation between correlation and response at long observation times but with a slope different from the bath temperature. This has been interpreted as a measure of the system’s “effective temperature.”

Despite the technological relevance of gels, understanding dynamic arrest in these soft matter systems is still lagging behind. Differently from glasses, where the non-ergodicity stems from crowding effects (caging), gels arrest due to the formation of a percolated network of bonds. Particles are now caged by bonds but, in the arrested state, can still participate in large-amplitude floppy modes of the network. This difference has important structural and dynamical consequences which have not been fully exploited. Experimental measurements of FDT violations have been performed on low-density colloidal systems, using dynamic light scattering [13], electrical [14] and rheological

[14–19] techniques, but the results (especially the electrical measurements) have been highly controversial. Abou and Gallet [18] have found violation of FDT using beads embedded in the Laponite sample, but more recent measurements [16] using a similar technique have not shown any violations of FDT over several decades in frequency. Greinert *et al.* [19] have reported an effective temperature larger than bath temperature for Laponite at late stages of aging, but the results are not conclusive. Indeed Jop *et al.* [20,21] have performed measurements using the same method without finding any evidence of violations of FDT. On the other hand, electrical measurements [14] show very large deviations, compatible with domain growth processes, although the interpretation of the results could be affected by the progressive dissolution of ions in solution. A clear interpretation of these results is still lacking and is complicated by the use of experimental samples which age under different mechanisms and are probably undergoing simultaneously gelation and phase separation. This is the case of Laponite, which can arrest both forming a gel or a glass [22,23].

In this Letter, we study for the first time FDT violations in a well-characterized model gel to shed light on this contradictory situation from a fundamental perspective. By studying different external perturbations, coupled to different channels for the decay of thermal fluctuations, we are able to show that violations do occur, but only for observables strongly coupled with the bond association process. The self-density fluctuations, which have been crucial in understanding FDT violation in glasses, do not show any violations in our calculations, providing evidence that diffusional processes in gels do not couple with the arrest mechanism. These results provide a concrete theoretical basis for (re)assessing and understanding the discrepancies in the existing results, and also for future experiments.

Methods.—We focus on a class of reduced valence systems whose equilibrium properties have been recently investigated in depth [24,25]. In such systems, gas-

liquid phase separation is confined to a tiny region in the temperature-density (T - ρ) plane [24,25], at low ρ and T , so that the slowing down of the dynamics upon cooling does not interfere with phase separation, providing a clean model system for investigating bond-driven arrest. Specifically, we study a binary mixture of bifunctional (N_2) and three-functional (N_3) hard-sphere particles of diameter σ whose surface is decorated by patches located on their surface. In the case of only two sites ($N_3 = 0$), the system self-assembles into equilibrium chains, whose equilibrium length is fixed by density and temperature. Adding a fraction of particles with three sites ($N_3 \neq 0$), cross-links between the chains take place at low temperature and the system evolves to form a spanning network [25]. We study different values of the relative concentration $x_2 \equiv N_2/(N_2 + N_3)$. The interaction potential between particles 1 and 2 depends both on the distance \mathbf{r}_{12} between the centers of the two particles and on their relative orientation Ω_{12} , $V(\mathbf{r}_{12}, \Omega_{12}) = V_{\text{c.m.}}(\mathbf{r}_{12}) + V_p(\mathbf{r}_{12}, \Omega_{12})$. $V_{\text{c.m.}}$ is the center of mass repulsion described by a steep potential and V_p models the site-site short-range attractive interaction. For a detailed description of the functional form see Ref. [26], where the model equilibrium structural and dynamical properties are studied in depth.

We perform both Brownian dynamics and Metropolis Monte Carlo calculations. The simulation procedure is the following. A configuration is first equilibrated at high temperature T_i and at time $t = 0$ the temperature of the bath is quenched at T_f . As the system ages, at time t' , a perturbation in the Hamiltonian is switched on, $\delta\mathcal{H} = -hB$, where B is a generic observable and h is the field strength. The system evolves in the presence of the perturbation field and the observable A (conjugated to the perturbation B) is measured at time t . The integrated response is defined as $\chi(t, t') = |\delta\langle A(t) \rangle_h / \delta h(t')|$. The correlations $C(t, t') = \langle A(t)B(t') \rangle$ are measured with the same protocol but without perturbing the system.

For aging materials, the following generalization of the fluctuation-dissipation theorem was suggested [5]:

$$\frac{\partial}{\partial t'} \chi(t, t') = -\frac{X(t, t')}{T} \frac{\partial}{\partial t'} C(t, t'). \quad (1)$$

$X(t, t')$ is the so-called fluctuation-dissipation ratio (FDR) which is unity at equilibrium. In glassy systems it measures the distance from equilibrium. The easiest and most commonly adopted procedure to measure $X(t, t')$ requires switching on the perturbation at time t' and measuring the response function at different times $t > t'$ (fixed- t' procedure), as shown schematically in Fig. 1(a). $X(t, t')$ is then taken as the slope of the parametric plot of $T\chi(t, t')$ versus $C(t, t')$. As discussed in Ref. [27], this procedure is correct only in systems with time translational invariance or where $X(t, t')$ is not an explicit function of t and t' . In the correct procedure the perturbation field has to be applied at different t' times while the response must be measured at fixed time t (fixed- t procedure), as shown in Fig. 1(b).

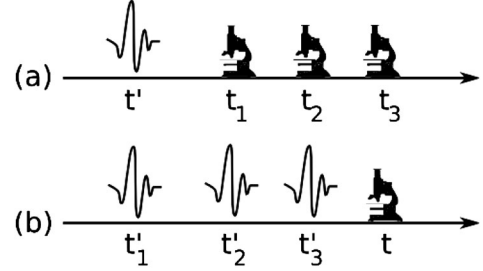


FIG. 1. Schematic representation of the two used protocols: (a) fixed- t' and (b) fixed- t . The perturbation, symbolically indicated as a wave, is switched on at time t' and the system's response (the microscope) is measured at time t . For both protocols, $t - t'$ is the time elapsed since the perturbation has been switched on.

We consider two different types of perturbations (and conjugated observables): The first perturbation acts directly on the system self-density at wave vector \mathbf{k} (as commonly done in previous calculation for glasses [7–10]),

$$\begin{aligned} A(t) &= N^{-1} \sum_j \epsilon_j \exp[i\mathbf{k} \cdot \mathbf{r}_j(t)], \\ B(t) &= 2 \sum_j \epsilon_j \cos[\mathbf{k} \cdot \mathbf{r}_j(t)], \end{aligned} \quad (2)$$

where ϵ_j is a bimodal random variable of mean 0 [28]. The associated correlation function is the self-intermediate scattering function, $F_s(t, t') = N^{-1} \sum \langle \exp[-i\mathbf{k} \cdot (\mathbf{r}_i(t) - \mathbf{r}_i(t'))] \rangle$. The second case is a perturbation acting directly on the particle's energy [29] (to probe bonding, since due to the short-range nature of the interaction the potential energy is a measure of the number of bonds),

$$A = B = \sum_i \epsilon_i E_i, \quad (3)$$

where E_i is the potential energy of the i th particle, defined as $E_i \equiv (1/2) \sum_j V(\mathbf{r}_{ij}, \Omega_{ij})$. Each couple of interacting particles (i, j) has its energy perturbed according to $V_p(\mathbf{r}_{ij}, \Omega_{ij}) = V(\mathbf{r}_{ij}, \Omega_{ij})[1 - h(\epsilon_i + \epsilon_j)]$, where $V_p(\mathbf{r}_{ij}, \Omega_{ij})$ is the potential energy after the perturbation is switched on. For Brownian simulations, this translates in all forces and torques between particle i and j being scaled by the factor $[1 - h(\epsilon_i + \epsilon_j)]$. For this choice of the variables $C(t, t') = \sum_i [\langle E_i(t)E_i(t') \rangle - \langle E_i(t) \rangle \langle E_i(t') \rangle]$ and $\chi(t, t') = \sum_i \epsilon_i (E_i - \langle E_i(t) \rangle) / \delta h$. Notice that in this case one is forced to use connected correlation functions [30], since the average value of the energy changes during the aging process.

Both perturbations, Eq. (2) and (3), are averaged over 100 independent realizations of the fields ϵ_i . To improve statistics, each measure is in addition averaged over 30 independent starting configurations. We have used field amplitudes equal to $h = 0.007$ for self-density perturbations and $h = 0.02$ for the energy perturbations. These

values have been selected after a careful verification of the linear regime.

Results.—We start by investigating the equilibrium-polymer case ($x_2 = 1$) with Brownian dynamics, starting from a high- T monomeric state, perturbing the self-density. After quenching to a low T the system starts to polymerize, as indicated by the growth of the fraction of bonds formed, p_b (see inset in Fig. 2). A fixed- t' self-density perturbation, Eq. (2) with $k\sigma = 1.9$, is applied during the aging process. We investigate different cases, switching on the perturbation at different times, corresponding to several different values of p_b . The resulting FD plot is reported in Fig. 2, showing that in all cases FDT is not violated, despite the nonequilibrium state of the system. We also study the case in which a fraction of three-functional particles is added, to provide branching point between different chains, resulting in a self-assembled network. Again, using the self-density perturbation, violation of the FDT are not observed, even when the perturbation is turned on after a percolating network has formed.

To make sure that the results obtained are not an artifact of the fixed- t' protocol, we repeat the same procedure with the more computationally expensive (but unbiased [27]) fixed- t protocol. We also test the dependence on the wave vector and the sensitivity to the microscopic dynamics by comparing Monte Carlo calculations and Brownian evolutions. In all cases, we confirm (see Fig. 3) that perturbation of the self-density does not result in an apparent violation in the FDT plot.

Results discussed so far show that, when self-density fluctuations are selected as a tool for investigating the FDT in chains and network forming systems, the resulting parametric plot does not reveal any apparent violation in the

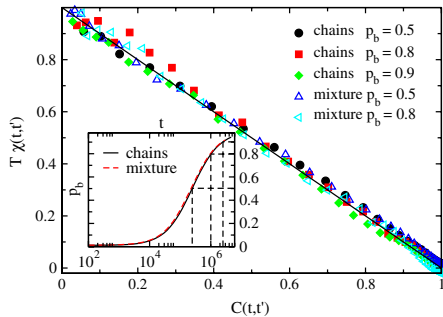


FIG. 2 (color online). FD plots for the $x_2 = 1$ (full symbols) and $x_2 = 0.8$ (open symbols) systems at $\phi = 0.026$. The systems are aging from $T_i = 0.15$ to $T_f = 0.04$ and a self-density perturbation (Eq. (2) with $k\sigma = 1.9$) is switched on when the fraction of bonds is p_b . The inset shows the time dependence of p_b during aging. The units are chosen so that $t = 1$ is the time it takes a particle to diffuse over a distance equal to its diameter (σ), while T are measured in units of the bond potential depth. Dashed lines indicate the times at which perturbations have been switched on. Note that, for the $x_2 = 0.8$ case, percolation occurs when $p_b = 0.79$ [26].

explored $k\sigma$ range. On the other hand, as alluded to before, in low-density systems, bonding is the relevant quantity controlling the slowing down of the dynamics and cages are not controlled by excluded volume effects. This suggests that energy can offer an indicator that is more strongly coupled to the arrest mechanism. To test this hypothesis we apply a perturbation to the particle's energy, Eq. (3), following Ref. [29], where violations of FDT were connected to the self-assembly efficiency in a model of virus capsids. Using the energy perturbation scheme, it is crucial to adopt the expensive fixed- t perturbation protocol.

Figure 4 shows the FD plot for energy perturbations, Eq. (3), for a series of quenches to different T_f , all starting from a monomeric state. All curves show large deviations and significantly differ from the results obtained for the self-density perturbation. At the largest T_f the system almost reaches equilibrium within the time explored in the simulation and the violation of FDT is only mild, especially at longer t' times [i.e., small $t - t'$ and $C(t, t')/C(t, t)$ close to unity]. At lower T_f the FDT violations become more pronounced. At sufficiently low T_f (for example, below $T_f = 0.08$ in Fig. 4), the FD plot deviates significantly from a straight line already at small $t - t'$ and becomes flat for longer $t - t'$. The window over which the function is flat increases as T_f is lowered. Such behavior is peculiar of coarsening systems [4,31,32]. At the lowest temperature, $T_f = 0.04$ (the same at which self-density perturbations of Fig. 3 are calculated), the response of the system is always constant, which means that the FDR is null [$X(t, t') = 0$].

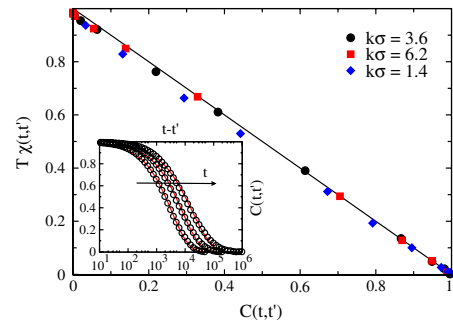


FIG. 3 (color online). FD plots for a system with $x_2 = 0.9$ at $\phi = 0.10$, using self-density perturbation, Eq. (2), at three values of $k\sigma$. The system is aged, with MC calculations, from $T_i = 1$ to $T_f = 0.04$ and data are collected when $p_b = 0.65$ (corresponding to 5×10^4 MC sweeps). The inset shows the self-density correlation functions for the same mixture aging from $T_i = 1$ to $T_f = 0.04$ for different times t ($t = 5 \times 10^4, 2 \times 10^5, 10^6$ MC sweeps) at $k\sigma = 3.6$. $F_s(t, t')$ shows a complex stretched-exponential relaxation (continuous lines), with a decay time increasing with t , and a fitted stretched exponent that decreases from 0.7 to 0.6. Note the absence of an intermediate time plateau. The same type of relaxation holds for the coherent scattering function [26].

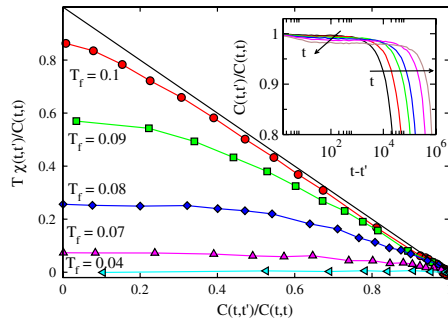


FIG. 4 (color online). FD plot for the $x_2 = 0.9$ system at $\phi = 0.10$ for the energy perturbation [Eq. (3)] for different T_f . Both correlation and response have been normalized by $C(t, t)$, which is independent of t' . The inset shows the energy correlation functions for the same mixture aging from $T_i = 1$ to $T_f = 0.04$ for different times t ($t = 5 \times 10^4, 10^5, 2 \times 10^5, 3 \times 10^5, 6 \times 10^5, 10^6$ MC sweeps). Energy correlations have a complex two-step relaxation. The height of the plateau decreases with increasing t , while its length increases as the system ages.

Our results provide an answer to the question raised with this Letter's title and a possible interpretation scheme for understanding the discrepancies in experimental results. In fact, we show that, in low-density arrested states, the choice of the perturbation is crucial in order to detect deviations from the equilibrium behavior. Differently from glasses, the relaxation dynamics accessed by density fluctuation does not provide information on the structural arrest. The diffusive motion of the clusters at the early stage of the aggregation process and the diffusive motion of wide regions of the network made possible by the floppiness of the structure at late stages significantly mask the out-of-equilibrium state. Under these conditions, self-density fluctuations are not a slow variable, despite their clear aging, explaining why in microrheological experiments [14–17]—where fluctuations in the positions of probe particles are measured—no violations are observed. Instead, the complex relaxation shows up if one considers the energy correlation function (inset of Fig. 4), and allows us to quantify the violations of FDT for these systems.

We recall that in charged colloidal systems (including Laponite) a perturbing electric field induces a polarization of the electric double layer [33], effectively modulating the dielectric constant and the electrostatic association between particles. In this respect, the perturbation in the bond we have implemented can be seen as a zeroth order model for describing the effect of weak electrical perturbations in colloidal systems. Hence it may not be a coincidence that FDT violations observed via electrical measurements [14] in Laponite are similar to the ones we have found when perturbing the bonds [$X(t, t') = 0$]. Interestingly, $X(t, t') = 0$ is the violation expected for coarsening systems, despite the fact that the aggregation process in the investigated model cannot, by construction, be attributed to an underlying phase separation.

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