Violation of the fluctuation-dissipation relation during the formation of a colloidal glass

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Abstract. – The relationship between the conductivity and the polarization noise is measured in a colloidal glass as a function of frequency in the range 1 Hz–40 Hz. It is found that at the beginning of the transition from a fluid-like sol to a solid-like colloidal glass the fluctuation-dissipation relation is strongly violated. The amplitude and the persistence time of this violation are decreasing functions of frequency. At the lowest frequencies of the measuring range it persists for times which are about 5% of the time needed to form the colloidal glass. This phenomenology is quite close to the recent theoretical predictions done for the violation of the fluctuation-dissipation relation in glassy systems.

Many physical systems in nature are not in thermodynamic equilibrium because they present very slow relaxation processes. A typical example of this phenomenon is the aging of glassy materials: when they are quenched from above their glass transition temperature $T_g$ to a temperature $T < T_g$, any response function of these systems depends on the aging time $t_a$ spent at $T$. For example, the dielectric and elastic constants of polymers continue to evolve several years after the quench [1]. Because of these slow relaxation processes, the glass is out of equilibrium, and usual thermodynamics does not apply. However, as this time evolution is slow, some concepts of the classical approach may be useful for understanding the glass aging properties. A widely studied question is how the temperature of these systems can be defined. One possible answer comes from the study of the deviation to the Fluctuation-Dissipation Relation (FDR) in an out-of-equilibrium system (for a review see, refs. [2–4]). In this letter we show that this approach is relevant for the study of a colloidal glass formation, where a strong violation of FDR is measured. Implications of this observation go beyond the physics interest. Indeed FDR is used as a tool to extract, from fluctuations measurements, several properties in biological, chemical and physical systems [5–7]. Our results indicate that before extending this smart technique to other systems, one has to carefully ensure that these systems are in equilibrium.

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In order to understand this new definition of temperature, we have to recall the main consequences of FDR in a system which is in thermodynamic equilibrium. We consider an observable $V$ of such a system and its conjugate variables $q$. The response function $\chi_{Vq}(\omega)$, at frequency $\nu = \omega/2\pi$, describes the variation $\delta V(\omega)$ of $V$ induced by a perturbation $\delta q(\omega)$ of $q$, that is $\chi_{Vq}(\omega) = \delta V(\omega)/\delta q(\omega)$. FDR relates the fluctuation spectral density of $V$ to the response function $\chi_{Vq}$ and the temperature $T$ of the system:

$$S(\omega) = \frac{2k_B T}{\pi \omega} \text{Im}[\chi_{Vq}(\omega)],$$

(1)

where $S(\omega) = \langle |V(\omega)|^2 \rangle$ is the fluctuation spectral density of $V$, $k_B$ is the Boltzmann constant, $\text{Im}[\chi_{Vq}(\omega)]$ is the imaginary part of $\chi_{Vq}(\omega)$. Textbook examples of FDR are Nyquist’s formula relating the voltage noise to the electrical resistance and Einstein’s relation for Brownian motion relating the particle diffusion coefficient to the fluid viscosity [8].

When the system is not in equilibrium, FDR, that is eq. (1), may fail. For example, violations of eq. (1) of about a factor of 2 have been observed in the density fluctuations of polymers in the glassy phase [9]. The first to propose that the study of the FDR violations are relevant for glassy systems was Sompolinsky [10]. This idea, which was generalized in the context of weak turbulence [11], has recently been reconsidered by Cugliandolo and Kurchan [12] and successively tested in many analytical and numerical models of glass dynamics [4,13–19]. Let us briefly recall the main and general findings of these models. Because of the slow dependence on $t_a$ of the response functions, it has been proposed that eq. (1) can be used to define an effective temperature of the system, specifically

$$T_{\text{eff}}(t_a, \omega) = \frac{S(t_a, \omega) \pi \omega}{\text{Im}[\chi_{Vq}(t_a, \omega)]2k_B}.$$  

(2)

It is clear that if eq. (1) is satisfied $T_{\text{eff}} = T$, otherwise $T_{\text{eff}}$ turns out to be a decreasing function of $t_a$ and $\omega$. The physical meaning of eq. (2) is that there is a time scale (for example $t_a$) which allows to separate the fast processes from the slow ones. In other words, the low-frequency modes relax towards the equilibrium value much slower than the high-frequency ones which rapidly relax to the temperature of the thermal bath. Therefore it is conceivable that the slow-frequency modes keep memory of higher temperatures for a long time and for this reason their temperature should be higher than that of the high-frequency ones. This striking behavior has been observed in several numerical models of aging [4,13–19]. Further analytical and numerical studies of simple models show that eq. (2) is a good definition of temperature in the thermodynamic sense [3,4]. In spite of the large amount of theoretical studies, there are only a few experiments which show a violation of FDR in real materials [9,20]. However these measurements are done at a single frequency and there is no idea on how the temperature relaxes as a function of time and frequency. The experimental analysis of the dependence of $T_{\text{eff}}(\omega, t_a)$ on $\omega$ and $t_a$ is very useful to distinguish among different models of aging: FDR violations are model dependent [4,13–19].

For these reasons we have experimentally studied the violation of eq. (1) during the colloidal glass formation in Laponite RD [21], a synthetic clay consisting of discoid charged particles. It disperses rapidly in water and solidifies even for very low mass fraction. Physical properties of this preparation evolve for a long time, even after the sol-gel transition, and have shown many similarities with standard glass aging [22,23]. Recent experiments [23] have proved that the structure function of Laponite at low concentration (less than 3% mass fraction) is close to that of a glass. As in our experiment the Laponite concentration is low, we call the solid-like Laponite solution either a colloidal glass or simply a glass.
Fig. 1 – Experimental set-up. The impedance under test $Z$ is a cell (diameter 7 cm, thickness 3 cm) filled with a 2.5 wt% Laponite sol. The electrodes of the cell are golden-coated to avoid oxidation. One of the two electrodes is grounded whereas the other is connected to the entrance of a low-noise voltage amplifier characterized by a voltage amplification $G$. With a spectrum analyzer, we alternately record the frequency response $\text{FR}(\omega) = \langle V_{\text{out}}/V_{\text{exc}} \rangle$ (switch $A$ closed) and the spectrum $S(\omega) = \langle |V_{\text{out}}|^2 \rangle$ (switch $A$ opened). The input voltage $V_{\text{exc}}$ is a white-noise excitation, thus from $\text{FR}(\omega)$ we derive the impedance $Z(\omega)$ as a function of $\omega$, that is $Z(\omega) = R_0/(G/\text{FR}(\omega) - 1)$; whereas from $S(\omega)$ we can estimate the voltage noise of $Z$, specifically $S_Z(\omega) = [S(\omega) - S_a(\omega)]/G^2$, where $S_a(\omega)$ is the noise spectral density of the amplifier.

In our experiment we measure the time evolution of the Laponite electrical properties during the colloidal glass formation. The solution is used as a conductive liquid between the two golden-coated electrodes of a cell (see fig. 1). The Laponite solution is prepared in a clean $\text{N}_2$ atmosphere to avoid $\text{CO}_2$ and $\text{O}_2$ contamination, which perturbs the electrical measurements. Laponite particles are dissolved at a concentration of 2.5% mass fraction in pure water under vigorous stirring during 20 min. To avoid the existence of any initial structure in the sol, we pass the solution through a 1 $\mu$m filter when filling our cell. This instant defines the origin of the aging time $t_a$ (the filling of the cell takes roughly two minutes, which can be considered the maximum inaccuracy of $t_a$). The sample is then sealed so that no pollution or evaporation of the solvent can occur. At this concentration, the light scattering experiments show that Laponite structure functions are still evolving 500 h after the preparation [22]. We only study the beginning of this glass formation process.

The two electrodes of the cell are connected to our measurement system, where we alternately record the cell electrical impedance $Z(t_a, \omega)$ and the voltage noise density $S_Z(t_a, \omega)$ (see fig. 1). Taking into account that in this configuration $\text{Im}[\chi V_q(t_a, \omega)] = \omega \text{Re}[Z(t_a, \omega)]$, one obtains from eq. (2) that the effective temperature of the Laponite solution as a function of aging time and frequency is

$$T_{\text{eff}}(t_a, \omega) = \frac{\pi S_Z(t_a, \omega)}{2k_B} \text{Re}[Z(t_a, \omega)];$$

which is an extension of the Nyquist formula.

In fig. 2a, we plot the real and imaginary part of the impedance as a function of the frequency $\nu$, for a typical experiment. The response of the sample is the sum of 2 effects: the bulk is purely conductive, the ions of the solution follow the forcing field, whereas the interfaces between the solution and the electrodes give mainly a capacitive effect due to the presence of
Fig. 2 – The response function. (a) Frequency dependence of a sample impedance for 2 different aging times: $t_a = 0.3\,\text{h}$, real (▲) and imaginary (△) part; $t_a = 24\,\text{h}$, real (●) and imaginary (○) part. The equivalent circuit for the cell impedance is shown in the inset: $Z$ is the sum of a resistive volume $R_b$ and a capacitive interface $C_s$ between the Laponite solution and the electrodes. The increase of $\text{Re}(Z)$ toward small frequencies ($\nu < \nu_c$) is due to the dissipative part of the capacitance (loss tangent $\simeq 0.2$). For $\nu > \nu_c$ the impedance of the cell is dominated by the bulk resistance $R_b$. (b) Time evolution of the bulk resistance. This long-time evolution is the signature of the aging of the sol. In spite of the decreasing mobility of Laponite particles in solution during the gelation, the electrical conductivity increases.

the Debye layer [24]. This behaviour has been validated using a four-electrode potentiostatic technique [25] to make sure that the capacitive effect is only due to the surface. In order to test only bulk properties, the geometry of the cell is tuned to push the surface contribution to low frequencies: the cut-off frequency of the equivalent R-C circuit is less than 0.6 Hz. The time evolution of the resistance of one of our samples is plotted in fig. 2b: it is still decaying in a non-trivial way after 24 h, showing that the sample has not reached any equilibrium yet. This aging is consistent with that observed in light scattering experiments [22].

As the dissipative part of the impedance $\text{Re}(Z)$ is weakly time and frequency dependent, one would expect from the Nyquist formula that so does the voltage noise density $S_Z$. But as shown in fig. 3, FDR must be strongly violated for the lowest frequencies and earliest times of our experiment: $S_Z$ changes by several orders of magnitude between highest values and the high-frequency tail [26]. This violation is clearly illustrated by the behavior of the effective temperature in fig. 4. For long times and high frequencies, the FDR holds and the measured temperature is the room one (300 K), whereas for early times $T_{\text{eff}}$ climbs up to $3 \cdot 10^5$ K at 1 Hz. Notice that the violation extends to frequencies much larger than the 0.6 Hz cut-off separating the volume from the surface effects. Moreover, the scaling presented in the inset of fig. 3 seems to indicate that $T_{\text{eff}}$ can be even larger for lower frequencies and lower aging times. Indeed, we found in all the tested samples no evidence of a saturation of this effective temperature in our measurement range. In order to be sure that the observed violation is not due to an artifact of the experimental procedure, we filled the cell with an electrolyte solution with the same $pH$ of the Laponite sol so that the electrical impedance of the cell was the same. In this case we did not observe any violation of FDR [27].

Let us now briefly discuss the results. The observed very large value of $T_{\text{eff}}$ is of course very striking. However the existence of infinite $T_{\text{eff}}$ was predicted [4] and numerically verified [16] in systems presenting domain growth process. This is probably the way in which the Laponite solution makes the transition towards the colloidal glass state. The influence of these domains
Fig. 3 – Fluctuations. Voltage noise density of one sample for different aging times. The strong increase of $S_Z$ for low frequencies is quite well fitted by a power law $\omega^\alpha$, with $\alpha = 3.3 \pm 0.4$. This effect is a decreasing function of time, and a good rescaling of the data with a $\omega t^\beta_a$ law can be achieved as shown in the inset for $\beta = 0.5 \pm 0.1$.

on the electrical conductivity of Laponite is related to the electrostatic interaction among the Laponite disks, which is a widely studied and not yet completely understood problem [28]. The physical origin of the large $T_{eff}$ certainly lays in these complex interactions. However one may wonder whether the observed $T_{eff}$ is mainly due to bulk effects or to a conductive phenomenon produced at the Debye layers on the electrodes. In our opinion the latter has to be excluded for two reasons. The first one is that the violation extends to frequencies much larger than the 0.6 Hz cut-off separating the volume from the surface effects. The second

Fig. 4 – Effective temperature. (a) Effective temperature as a function of frequency for different aging times [29]. We restrict the frequency range to 1 Hz to limit the surface contribution to the measurement. As $S_Z$ in fig. 3, $T_{eff}$ is strongly increasing for low frequencies and short aging time. (b) Time-frequency representation of the effective temperature of the same experiment. $T_{eff}$, coded with a logarithmic grey scale, is reaching huge values in the short aging time/low frequency corner. This large violation is observed in numerical simulations of systems presenting domain growth processes which are probably good models to describe the formation of a Laponite gel.
The reason is that complementary measurements, done in cells with different geometries, show that for frequency larger than the cut-off $\nu_c$, the effect of the Debye layers on the violation is negligible [27].

The comparison with the results of the other experiments [9,20] is difficult because these two experiments are done in different materials and at a single frequency. Thus in these two experiments it is impossible to know the evolution of the violation both in frequency and time. Furthermore the violation observed in these experiments is of order one, whereas in our experiment it is several order of magnitudes. However our experiment and the one on supercooled fluid [20] have a common important result, which merits to be stressed. The violation of FDR at frequency $\omega$ persists for times which are several orders of magnitude larger than the time $1/\omega$, which is often considered as the characteristic time of the violation of FDR at frequency $\omega$.

In conclusion, we have observed for the first time that at the beginning of the transition from a fluid-like sol to a glass FDR is strongly violated. As predicted by the theory the amplitude and the persistence time of this violation are decreasing functions of frequency. These large violations are observed in numerical simulations of systems presenting domain growth processes which are probably good models to describe the formation of a Laponite gel. At the moment we are unable to claim whether in our system $T_{\text{eff}}$ can be seen as a temperature in the thermodynamic sense: other kinds of measurements will be necessary to do such a statement. The observed violation is very important from the application point of view because FDR can be invoked to estimate the response from a measurement of fluctuations. Our results show that this technique, although very powerful, could give in some cases a result which is not very accurate.

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