Experimental study of the Fluctuation-Dissipation-Relation during an aging process

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Abstract

The validity of fluctuation dissipation relations in an aging system is studied in a colloidal glass during the transition from a fluid-like to a solid-like state. The evolution of the rheological and electrical properties is analyzed in the range $1 \text{Hz} - 40 \text{Hz}$. It is found that at the beginning of the transition the fluctuation dissipation relation is strongly violated in electrical measurements. 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. In contrast in the rheological measurements no violation of the fluctuation dissipation relation is observed. The reasons of this large difference between the electrical and rheological measurements are discussed.

1 Introduction

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. 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 ref. [2, 3, 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, 6, 7]. Our results indicate that before extending this smart technique to other systems, one has to carefully ensure that these systems are in equilibrium.

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 $\chi_{V q}(\omega)$, 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 $\chi_{V q}(\omega) = \delta V(\omega)/\delta q(\omega)$. FDR relates the fluctuation spectral density of $V$ to the response function $\chi_{V q}$ and the temperature $T$ of the system:

$$S(\omega) = \frac{2k_B T}{\pi \omega} \text{Im} \left[ \chi_{V q}(\omega) \right]$$

where $S(\omega) = \langle |V(\omega)|^2 \rangle$ is the fluctuation spectral density of $V$, $k_B$ is the Boltzmann constant, $\text{Im} \left[ \chi_{V q}(\omega) \right]$ is the imaginary part of $\chi_{V q}(\omega)$. Textbook examples of FDR are Nyquist’s formula relating the voltage noise to the electrical resistance and the 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 about a factor of 2, of eq.1 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 been recently 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:

$$T_{\text{eff}}(t_a, \omega) = \frac{S(t_a, \omega) \pi \omega}{\text{Im} \left[ \chi_{V q}(t_a, \omega) \right] 2k_B}$$

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 function of time and frequency. The experimental analysis of the dependence of $T_{eff}(\omega, t_a)$ on $\omega$ and $t_a$ is very useful to distinguish among different models of aging: FDR violations are model dependent [14]-[19].

For these reasons we have experimentally studied the violation of eq.4 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 evolves 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.

In our experiment we measure the time evolution of the Laponite electrical and rheological properties during the colloidal glass formation. The paper is organized as follows. In the next section the electrical measurements are described. Rheological measurements are discussed in section 3. Finally we conclude in section 4.

2 Electrical measurements

2.1 The experimental apparatus

The Laponite 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 N$_2$ atmosphere to avoid CO$_2$ and 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 20min. To avoid the existence of any initial structure in the sol, we pass the solution through a 1µm 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 500h 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 $Im \left[ \chi_{Vq}(t_a, \omega) \right] = \omega Re \left[ Z(t_a, \omega) \right]$, one obtains from eq.2 that the effective temperature of the Laponite solution as a function of the aging time and frequency is:

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

which is an extension of the Nyquist formula.
**2.2 Experimental results**

In Fig.2(a), 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 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 cutoff frequency of the equivalent R-C circuit is less than 0.6 Hz. The time evolution of the resistance of one of our sample is plotted in Fig.2(b): it is still decaying in a non trivial way after 24h, 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 $Re(Z)$ 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
Figure 2: The response function (a) Frequency dependence of a sample impedance for 2 different aging time: $t_a = 0.3h$, real (▲) and imaginary (△) part; $t_a = 24h$, 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 $Re(Z)$ 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.

In high frequencies, the FDR holds and the measured temperature is the room one ($300K$); whereas for early times $T_{eff}$ climbs up to $3.10^5K$ at $1Hz$. Notice that the violation extends to frequencies much larger than the $0.6Hz$ cutoff separating the volume from the surface effects. Moreover, the scaling presented in inset of Fig. seems to indicate that $T_{eff}$ 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
Figure 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 $\omega t^\beta$ law can be achieved as shown in the inset for $\beta = 0.5 \pm 0.1$.

an artifact of the experimental procedure, we filled the cell with an electrolyte solution with pH close to that of the Laponite sol such that the electrical impedance of the cell was the same. Specifically we filled the cell with NaOH solution in water at a concentration of $10^{-3}$ mol.l$^{-1}$. The results of the measurements of $T_{eff}$ are shown in fig.5 at two different time after the sample preparation. In this case we did not observe any violation of FDR at any time.
Figure 4: **Effective temperature of Laponite** Effective temperature as a function of frequency for different aging times [27]. We restrict the frequency range to 1 Hz to limit the surface contribution to the measurement. As $S_Z$ in Fig. 3, $T_{\text{eff}}$ strongly increases and reaches huge values for low frequencies and short aging times. This large violation is observed in numerical simulations of systems presenting domain growth process.

Figure 5: **Effective temperature of an NaOH solution in water.** The effective temperature is plotted as a function of frequency for two different times after the preparation. This solution has a pH close to that of the Laponite, but no violation is observed in this case for any aging time.
2.3 Discussion

Let us now briefly discussed the results. The observed very large value of $T_{eff}$ is of course very striking. However the existence of infinite $T_{eff}$ was predicted \[4\] and numerically verified \[15\] 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 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 $0.6\,Hz$ cutoff separating the volume from the surface effects. The second reason is that complementary measurements, done in cells with different geometries, show that for frequency larger than the cutoff $\nu_c$ the effect of the Debye layers on the violation is negligible.

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 order of magnitude larger then the time $1/\omega$, which is often considered as the characteristic time of the violation of FDR at frequency $\omega$.

3 Rheological Measurements

In the previous section we have shown that the FDR is strongly violated by the electrical properties of Laponite. We want to understand whether a violation can be observed in the measurements of other physical properties. Of course there are no reasons to assume that $T_{eff}$ is the same for all the variables but the differences and the analogies found in the evolution of $T_{eff}$ obtained by the measurements of several variables may give new insight on aging theories and on the coupling of the different variables in an aging material. Therefore we performed rheological measurements on Laponite and we checked FDR in these measurements.

3.1 Experimental apparatus

To achieve this result we built a new rheometer which is sensitive to thermal fluctuations. The principle of the rheological measurement is a standard one and is illustrated in fig.3. We describe here only the main features, more details can be found in ref.\[29\]. A rotor of diameter 12mm is inserted in a cylindrical cell. The gap of 1mm between the rotor surface and the cell is filled with the fluid under study. The rotor is suspended by two steel wires. On the top of the rotor we fixed an optical prism. This prism is part...
of a Nomarski interferometer [30] which is used to measure the rotation angle $\theta$ of the rotor. The sensitivity of this system is better than $10^{-10}\text{ rad}/\sqrt{\text{Hz}}$ corresponding to a torque on the rotor of about $10^{-13}\text{ N} \cdot \text{m}/\sqrt{\text{Hz}}$. An external torque $\Gamma_{\text{ext}}$ can be applied to the rotor by using the electrostatic interaction of a capacitor (see fig.6). One of the two electrodes of the capacitor is fixed on the rotor whereas the other is fixed on the cell walls. When a voltage difference $V_c$ is applied on this capacitor the attractive force between these two electrodes produces a torque on the rotor which is equilibrated by the stiffness of the steel wires.

Figure 6: **Rheometer** Vertical (a) and horizontal (b) cross section of the rheometer. The torque is applied through the electrostatic interaction of electrodes $A_{1,2}$ and $B_{1,2}$ when the voltage $V_c$ is applied to this capacitor.

Let us consider the simple case of a Newtonian fluid of viscosity $\eta$. The response of this torsion pendulum in Fourier space is

$$\chi_{\theta \Gamma_{\text{ext}}} = \frac{\delta \theta}{\Gamma_{\text{ext}}} = \frac{1}{(k - J\omega^2) - i\alpha \eta \omega} \quad (4)$$

where $J$ is the rotor inertia moment, $k$ the steel wires stiffness and $\alpha$ is a geometric factor.

In the experiment we have access to two quantities: the angular position $\theta$ of the rotor, and the voltage $V_c$ driving the torque. $\Gamma_{\text{ext}}$ being quadratic in $V_c$, we add a constant offset to it in order to linearise this relation. For small displacements, the response function $\chi_{\theta \Gamma_{\text{ext}}}$ is then simply proportional to $\chi_{\theta V_c}$. The missing constant can be found by performing an inertial calibration of the response: the real part of $1/\chi_{\theta \Gamma_{\text{ext}}}$ is a parabola whose quadratic coefficient is the rotor inertia moment $J$. $J$ is known with a good precision, and thus can be used to calibrate the measurement.
This rheometer has been tested using a silicon oil with $\eta = 2 Pa s$. We first measure the response by using a white noise voltage excitation for $V_c$ with an amplitude corresponding to a torque $\Gamma_{ext} \simeq 10^{-10} N m/\sqrt{Hz}$. The real and imaginary part of $1/\chi_{\theta_{ext}}$ are plotted as a function of frequency in fig.7(a) and fig.7(b) respectively. We see that in agreement with eq.4 the real part of $1/\chi_{\theta_{ext}}$ is very well fitted by a parabola whereas the imaginary part is linear for small $\nu$. The deviation of the data from the linear behaviour is due to the non-newtonian character of the silicon oil at higher frequencies. Once the response is known one can set the external torque to zero and measure $S_{\theta}$, the spectrum of the thermal fluctuations of $\theta$. In this case the fluctuation dissipation relation is:

$$S_{\theta} = \frac{4k_B T}{\omega} Im(\chi_{\theta_{ext}})$$  \hfill (5)

By inserting the measured $\chi_{\theta_{ext}}$ in eq.5, we get an estimation of the fluctuation spectrum $S_{\theta}$. The comparison between this computed $S_{\theta}$ and the measured one is done in fig.8. Except for the existence of the peaks due to environmental noise the agreement is quite good. Thus the rheometer has enough sensitivity to verify FDR in viscous fluids.

![Figure 7](image)

Figure 7: Response of the rheometer to a white noise excitation. The real (a) and imaginary (b) part of $1/\chi_{\theta_{ext}}$ are plotted as a function of frequency. The rheometer is filled with a viscous oil with $\eta = 2 Pa s$. The dashed curve in (a) corresponds to a quadratic fit of the data, and allows inertial calibration of the measurement (see text for details). The dashed line in (b) is a linear fit of low frequency data, it is consistent with a newtonian behavior of the fluid.

### 3.2 Measure on Laponite

We have studied the rheological properties of Laponite at 3% mass concentration in water. Laponite has been prepared in the way described in section 2) for electrical measurements and the rheometer is mounted inside a container filled with a clean Nitrogen atmosphere. Moreover, a thin oil layer on top of the Laponite solution ensures
no evaporation can occur. We first measure the response at different times $t_w$ after the preparation. The measured elastic and viscous modules of Laponite are plotted as a function of frequency in fig.9 (a) and (b) respectively. We clearly see that at short $t_w$ the liquid like solution has only viscous response. As time goes on an elastic modulus appears and the viscosity grows of about one order of magnitude. After 24 hours the solution has a solid like aspect with a viscoelastic response. The measurement the thermal fluctuation spectrum $S_\theta$ averaged on the first hour of the aging processes of Laponite is plotted in fig.10. The peak at 1.5 Hz has no physical meaning and is due to a mechanical resonance of the table. Whereas the resonance at 7 Hz is the resonant frequency of the torsion pendulum of the rheometer. The measure is compared to the prediction of the fluctuation dissipation theorem by inserting in eq.10 the measured values of the Laponite viscous response and $T = 300K$. We also inserted in eq.10 the effective temperature obtained by the electrical measurements averaged on the first hour. We clearly see that in the case of rheological measurements no violation of FDR can be detected within experimental errors. If a violation exists, it is much smaller than that observed in the electric measurements.

4 Discussion and Conclusion

We have studied the fluctuation dissipation relations during the transition of Laponite from a fluid-like state to a solid-like colloidal glass using electric and rheological measurements. Strong aging properties have been observed both in the electrical and rheological response functions. The behaviour of thermal fluctuations is instead quite different. In electric measurements a large violation of the dissipation fluctuation relation is observed at the beginning of the transition from a fluid like sol to a glass. As
predicted by the theory the amplitude and the persistence time of this violation are decreasing functions of frequency. The observed effective temperature reaches $10^5 K$ for frequencies smaller than $1 Hz$. This violation involves frequencies which are much larger than $1/t_w$. Instead in the rheological measurements no detectable violation of
the fluctuation dissipation relation has been observed. The reasons of this behaviour and of such a big difference between the two physical properties are not understood. The first striking result is the very high effective temperature measured in the electrical properties. These very high effective temperatures has been observed in the numerical simulation of aging models presenting domain growth. Thus this behaviour of electrical properties of laponite could be explained by the formation of large domains during the transition toward the colloidal glass state. However one wonders whether the growth of these domains does not affect the fluctuations in the rheological measurements. Another possible explanation of the large $T_{eff}$ in electric measurements is the dissolution of aggregated particles and consequently of ions in the Laponite-water solution. It is conceivable that this effect should not influence the rheological measurements. The second striking result, which merits to be discussed, is the fact that in electric measurements the violation involves frequencies which are much larger than $1/t_w$. This results agrees with the experiment of ref.[20] but it is different from what is theoretically predicted and computed in numerical simulation. This observation leads us to another possible explanation of the discrepancy between electrical and rheological properties of Laponite. Indeed the time scale of relaxation of the fluctuations could not be the same for the two properties. At the moment we have not a clear and precise answer to this problem and more precise measurements are necessary in order to understand this large difference between rheological and electrical measurements.

The results of this paper are certainly preliminary but they show that the measurements of FDR in aging systems can give more insight to the problem of material aging. Indeed aging has been always characterized only by the measurements of the response function. We have shown here that the association of this measurement to that of the thermal fluctuations may show new and unattended aspects of an aging material.

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