# Aging and effective temperatures near a critical point

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(Dated: October 8, 2008)

The orientation fluctuations of the director of a liquid crystal(LC) are measured after a quench near the Fréedericksz transition, which is a second order transition driven by an electric field. We report experimental evidence that, because of the critical slowing down, the LC presents, after the quench, several properties of an aging system, such as power law scaling versus time of correlation and response functions. During this slow relaxation, a well defined effective temperature, much larger than the heat bath temperature, can be measured using the fluctuation dissipation relation.

PACS numbers: 05.40.-a, 05.70.Jk, 02.50.-r, 64.60.-i

The characterization of the thermodynamic properties of out of equilibrium and of slow relaxing systems is an important problem of great current interest which is studied both theoretically and experimentally. One of the main questions which has been investigated in the recent years is how a temperature can be defined for these out of equilibrium systems, mainly in the context of aging glasses, whose relaxation is nonexponential and extremely slow. Indeed when a glass is quenched from above to below the glass transition temperature its physical properties depend on the waiting time $t_w$ spent after the quench at the low temperature $T$. For these materials it has been proposed that a "good definition" (in the thermodynamic sense) of an effective temperature, $T_{\rm eff}$ can be obtained by the so called fluctuation dissipation relation (FDR) which is an extension of the fluctuation dissipation theorem (FDT) for an out of equilibrium system [1]. This $T_{\rm eff}$ is a function of the age of the system and of the observational time scale. To be more precise, let us consider an observable $\theta$, its conjugated variable $\Gamma$ and the integrated response, $\chi(t,t_w)$, of $\theta(t)$, at time $t$, to a Heaviside perturbation given to $\Gamma$ at a time $t_w < t$. This integrated response is related to the correlation function $C(t,t_w)$ of the thermal fluctuations $\delta\theta$ of $\theta$ by the FDR in the following way:

$$\chi(t,t_w) = \frac{1}{k_{\rm B}\ T_{\rm eff}(t,t_w)}[C(t,t) - C(t,t_w)] \qquad (1)$$

where $k_{\rm B}$ is the Boltzmann constant. Of course at equilibrium $T_{\rm eff} = T$ and both $\chi(t,t_w)$ and $C(t,t_w)$ depend only on $t - t_w$. For several models of aging dynamics it has been shown that the $T_{\rm eff}$ defined from eq. 1 is characterized by only two temperatures and a characteristic time, $t^*$, such that for $(t-t_w) > t^*$ then $T_{\rm eff} > T$ whereas for $(t-t_w) < t^*$, $T_{\rm eff} = T$ [1, 2]. However in experiments the results are less clear and the relevance for real materials of the $T_{\rm eff}$ as defined by eq. 1 is still an open question, which merits to be investigated [3, 4, 5]. The point is that in general it is very difficult to find simple theoretical models which can be directly compared with experiments. The recent theoretical works on aging at critical point are very useful in this sense. Indeed it has been recently shown that a system which is quenched at the critical point of a second order phase transition shares several properties observed in the relaxation dynamics of an aging glass [6, 7, 8]. For this reason this kind of behavior has been named "aging at critical point". The theoretical predictions on this critical systems are very useful because they can be a real benchmark to compare theory with experiment. The purpose of this letter is to report on experimental results on a critical system, which is, on a first approximation, described by a Ginzburg-Landau equation. Thus many results can be directly compared to theory but at the same time as all new experimental measurements they open new theoretical perspectives. From a general point of view the main result of our investigation is that after a quench at the critical point the system presents a violation of the fluctuation dissipation theorem and that for long correlation times a well defined $T_{\rm eff}$ can be defined from eq. 1.

The system of our interest is the Fréedericksz transition of a liquid crystal (LC), submitted to an electric field $\vec{E}$ [9, 10]. In this system, we measure the variable $\zeta$ which is the spatially averaged alignment of the LC molecules, whose local direction of alignment is defined by the unit vector $\vec{n}$. Let us first recall the general properties of the Fréedericksz transition. The system under consideration is a LC confined between two parallel glass plates at a distance $L = 9$ $\mu$m. The inner surfaces of the confining plates have transparent Indium-Tin-Oxyde (ITO) electrodes, used to apply the electric field. Furthermore the plate surfaces, are coated by a thin layer of polymer mechanically rubbed in one direction. This surface treatment causes the alignment of the LC molecules in a unique direction parallel to the surface (planar alignment),*i.e.* all the molecules have the same director parallel to $x$-axis. The cell is next filled by a LC having a positive dielectric anisotropy (p-pentylcyanobiphenyl, 5CB, produced by Merck). The LC is submitted to an electric field perpendicular to the plates, by applying a voltage $V$ between the ITO electrodes, *i.e.* $E = V/L$. In order to avoid electrodynamics effects of the

motion of the ions invariably present in the liquid crystal, we apply an AC voltage at a frequency $f_V = 1$ kHz ($V = \sqrt{2}V_0 \cos(2\pi f_V t)$) [9, 10]. More details on the experimental set-up can be found in ref.[11, 12]. When $V_0$ exceeds a threshold value $V_c$ the planar state becomes unstable and the LC molecules, except those anchored to the glass surfaces, try to align parallel to the field, *i.e.* the director, away from the confining plates, acquires a component parallel to the applied electric field ($z$-axis). This is the Fréedericksz transition whose properties are those of a second order phase transition [9, 10]. For $V_0$ close to $V_c$ the motion of the director is characterized by its angular displacement $\theta$ in $xz$-plane ($\theta$ is the angle between the $x$ axis and $\vec{n}$), whose space-time dependence has the following form : $\theta = \theta_0(x, y, t) \sin\left(\frac{\pi z}{L}\right)$ [9, 10, 13]. If $\theta_0$ remains small then its dynamics is described by a Ginzburg-Landau equation and one expects mean-field critical phenomena [9, 10, 13], in which $\theta_0$ is the order parameter and $\epsilon = \frac{V_0^2}{V_c^2} - 1$ is the reduced control parameter. We define the variable $\zeta$ as the spatially averaged alignment of the LC molecules and more precisely :

$$\zeta = \frac{2}{L}\frac{1}{\mathcal{A}} \iint_{\mathcal{A}} \mathrm{d}x\mathrm{d}y \int_0^L (1 - n_x^2)\mathrm{d}z \qquad (2)$$

where $\mathcal{A} = \pi D_0^2/4$ is the area, in the ($x$, $y$) plane, of the measuring region of diameter $D_0$, which is about 2 mm in our case. If $\theta_0$ remains small, $\zeta$ takes a simple form in terms of $\theta_0$ ($n_x = \cos(\theta)$) : $\zeta = 1/\mathcal{A} \iint_{\mathcal{A}} \mathrm{d}x\mathrm{d}y\theta_0^2$. The variable $\zeta$ is measured using the anisotropic properties of the LC, *i.e.* the cell is a birefringent plate whose local optical axis is parallel to $\vec{n}$. This optical anisotropy can be precisely estimated by measuring the phase shift $\Phi$ between two linearly polarized beams which cross the cell, one polarized along x-axis (ordinary ray) and the other along the y -axis (extraordinary ray). It can be shown that $\zeta = a + b\Phi$ where $a$ and $b$ are known coefficients (see ref. [11, 12] for details). The phase $\Phi$, measured by an interferometer [14], is acquired with a resolution of 24 bits at a sampling rate of 16384 Hz and then low pass filtered at 500 Hz in order to suppress the AC voltage at $f_V$. The instrumental noise of the apparatus is three orders of magnitude smaller than the amplitude $\delta\Phi$ of the fluctuations of $\Phi$ induced by the thermal fluctuations of $\zeta$. It has been shown that $\zeta$ is characterized by a mean value $\langle\zeta\rangle \propto \epsilon$, by a divergent relaxation time $\tau = \tau_o/\epsilon$ and by fluctuations which have a Lorentzian spectrum [12, 15].

In this letter, we consider the dynamic of $\zeta$ as a function of time after a quench from $\epsilon = \epsilon_1 > 0.3$ to $\epsilon = \epsilon_0 << 0.1$. The fact that the control parameter is the electric field allows one to have extremely fast quenches, typically 2 ms. Furthermore the typical relaxation time $\tau$ of $\zeta$ is about $10s$, at $\epsilon_0 \simeq 0$. This means that we can follow the out of equilibrium dynamics for about 4 order of magnitude in time. This relaxation dynamics, which lasts only a few seconds, allows us to repeat the experiment several times and to perform an ensemble average (indicated by $< . >$) of the measured quantities. We describe here a specific case of a quench from $\epsilon_1 = 0.3$ to $\epsilon_0 = 0.01$ (more details for other quenches will be given in a longer reports). The typical mean value $< \zeta(t) >$ of $\zeta$ after this quench is plotted in fig. 1 as a function of time $t$ ($t = 0$ is the time when the quench has been performed). This mean dynamics of $\zeta$ is obtained by repeating the same quench several times (7000 times). The behavior of $< \zeta >$ remains constant for a certain time and then slowly relaxes (see fig. 1b). Above a characteristic time which is about 0.2 s in our case, the relaxation becomes exponential. This behavior can be modelled by the equation of momentum [13], which neglecting the dependence on $(x, y)$ of $\theta_0$ is:

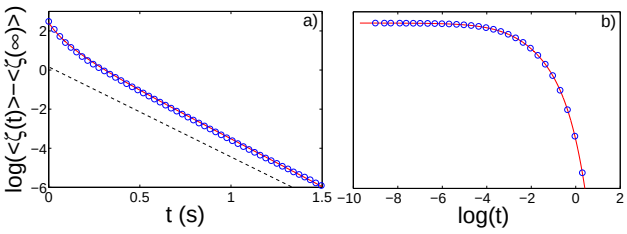



FIG. 1: a) Logarithm of the mean relaxation of the system, $\log\langle\zeta(t)\rangle$, as a function of time after a quench ($\circ$) from $\epsilon_1 = 0.3$ to $\epsilon_0 = 0.01$. The continuous line represent the theoretical response based on eq. 3 with $\langle\zeta\rangle \simeq \psi_0^2$. Dashed line is an exponential relaxation. b) Logarithm of the mean relaxation of the system as a function of the logarithm of time. The continuous line represent the theoretical relaxation.

$$\frac{\gamma\mathcal{A}L}{2}\frac{\mathrm{d}\theta_0}{\mathrm{d}t} = B\left[\, 2\,\epsilon\,\theta_0 - (\kappa + \epsilon + 1)\,\theta_0^3\right] + \eta \qquad (3)$$

where $\gamma$ is a viscosity coefficient, $B = \mathcal{A}\pi^2 K_1/4L$, $\kappa = (K_3 - K_1)/K_1$ and $K_1$, $K_2$ and $K_3$ are the three elastic constants of the LC. $\eta$ is a thermal noise delta-correlated in time, such that: $\langle\eta(t)\rangle = 0$ and $\langle\eta(t_1)\eta(t_2)\rangle = k_B T\gamma\mathcal{A}L\delta(t_2 - t_1)$. We decompose the dynamics of $\theta_0$ in a mean dynamics after the quench and its fluctuations, i.e. $\theta_0 = \psi_0(t) + \delta\theta_0$, where $\psi_0(t) = \langle\theta_0(t)\rangle$. The dynamics of $\Psi_0$ obtained from the analytical solution of eq.3 is shown in fig.1 as a continuous line, which perfectly agrees with the measured dynamics. The experimental data and the solution of eq.3 have two well distinguish limits : for $t \gg \tau \equiv \tau_0/(2\epsilon)$, the relaxation is exponential ($\tau \simeq 0.22s$ at $\epsilon_0 = 0.01$) ; for $t \ll \tau \equiv \tau_0/(2\epsilon)$, the dynamics of $\psi_0$ is almost algebric : $\psi_0(t) = \left[(\kappa + 1)\left(\frac{t}{\tau_0} + \frac{1}{(\kappa+1)\psi_0(0)}\right)\right]^{-1/2}$. This behavior is identical to the relaxation at the critical point [7]. Thus, the system should present aging phenomena in the limit $t \ll \tau$.

In our experimental system, we want to measure both the correlation function of the thermal fluctuations $\delta\theta_0$ of $\theta_0$, $C_\theta(t, t_w) \equiv \langle\delta\theta_0(t)\delta\theta_0(t_w)\rangle$, and the integrated re-

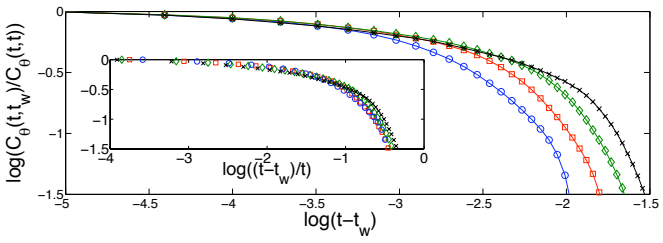



FIG. 2: a) Correlations functions $C_\theta(t,t_w)$ as a function of $t-t_w$ for different fixed $t = 0.2$ ($\circ$), 0.26 ($\Box$), 0.28 ($\diamond$) and 0.31 ($\times$) after the same quench of fig. 1. Inset: The correlation functions have a simple master curve obtained by plotting $C_\theta(t,t_w)/C_\theta(t,t_w)$ versus $(t-t_w)/t$.

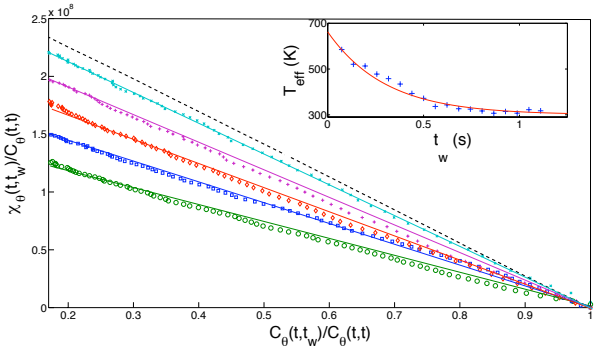



FIG. 3: Parametric plot integrated response versus correlation for $t_w = 0.19$ s ($\circ$), 0.31 s ($\Box$), 0.37 s ($\diamond$), 0.43 s ($+$), 0.56 s ($\times$). Continuous line are linear fits. Dashed line represents the Fluctuation-Dissipation Theorem at equilibrium. Inset : value of the effective temperature, obtained by a linear fit of the FD plots, as a function of the age of the system.

sponse function $\chi(t,t_w)$ of $\theta_0$, at time $t$ to a perturbation, given at time $t_w$, to its conjugated external field, with $t_w < t$. In equilibrium $\chi(t,t_w)$ and $C_\theta(t,t_w)$ depends only on the difference $t-t_w$ which is not the case here because the system is out of equilibrium.

To compute $\chi(t,t_w)$ and $C_\theta(t,t_w)$ in our experiment one has to consider that the measured variable is $\zeta$. As the area of the measuring beam is much larger than the correlation length, the global variable measured by the interferometer is $\zeta = \frac{1}{\mathcal{A}}\iint \theta_0^2 \mathrm{d}x\mathrm{d}y \simeq \psi_0^2 + 2\psi_0\delta\theta_0$. Thus the mean value of $\zeta$ is $\langle\zeta(t)\rangle = \psi_0^2(t)$ and the fluctuations of $\delta\zeta$ of $\zeta$ can be related to the fluctuations of $\theta_0$ : $\delta\zeta(t) = 2\psi_0(t)\delta\theta_0(t)$. The autocorrelation function of $\theta_0$ is obtained using the values of $\psi_0(t)$ and $\psi_0(t_w)$, *i.e.* $C_\theta(t,t_w) = \langle\zeta(t)\zeta(t_w)\rangle/(4\psi_0(t)\psi_0(t_w))$. The $C_\theta(t,t_w)$, measured at various fixed $t$, are plotted as function of $t-t_w$ in fig.2. We see that a simple scaling of the correlation function can be obtained by plotting them as a function of $(t-t_w)/t$. Notice that such a kind of scaling is typical for aging systems( see for example [2, 16]) Thus in agreement with theoretical predictions our system presents aging properties during the slow relaxation after a quench. The response function is obtained by applying a small change of the voltage $V_0$, which modifies the control parameter, *i.e.* $\epsilon = \epsilon_0 + \delta\epsilon$. First, we have to define the external torque conjugated to $\theta_0$. We separate $\theta_0(t)$ into the average part $\psi_0(t)$, solution of eq. 3 and a deviation $\Delta(t)$ due to $\delta\epsilon$ : $\theta_0(t) = \psi_0(t) + \Delta(t)$. If the response is linear, the average value of $\Delta$ is proportional to $\delta\epsilon$. In this limit, the equation of momentum can be rewritten :

$$\frac{\gamma\mathcal{A}L}{2}\frac{\mathrm{d}\Delta}{\mathrm{d}t} = B\left[2\ \epsilon_0 - (\kappa+\epsilon_0+1)3\psi_0^2\right]\ \Delta + \\ +\ 2\ B\ \delta\epsilon\ \psi_0(t)\left(1-\frac{\psi_0^2(t)}{2}\right) + \eta + O(\Delta^2) \qquad (4)$$

The external torque, and so the conjugated variable to $\theta_0$, is equal to :

$$\Gamma_{\mathrm{ext}} = 2B\ \delta\epsilon\ \psi_0(t)\ \left(1-\frac{\psi_0(t)^2}{2}\right) \qquad (5)$$

We define the linear response function $R(t,t_w) = <\Delta> /\Gamma_{\mathrm{ext}}$ of $\theta_0$ to $\Gamma_{ext}$ using a Dirac delta function for $\delta\epsilon$ at an instant $t_w$, *i.e.* $\delta\epsilon(t) \propto \delta(t-t_w)$. In the experiment the Dirac delta function is approximated by a triangular function of amplitude $\delta\epsilon_0$ and duration $\tau_r \simeq 2ms << \tau$, specifically: $\delta\epsilon = \delta\epsilon_0(1-2|t-t_w|/\tau_r$ for $|t-t_w| < \tau_r/2$ and $\delta\epsilon = 0$ for $|t-t_w| > \tau_r/2$, with $\tau_r/\tau \simeq 10^{-4}$. The measured quantity is the response $R_{\zeta,\delta\epsilon} = <\Delta\zeta> /\delta\epsilon$, of $\zeta(t)$ to $\delta\epsilon(t_w)$. As $\Delta\zeta(t) = 2\psi_0(t)\Delta$ it follows that the linear response of $\theta_0$ to $\Gamma_{ext}$ is:

$$R(t,t_w) = \frac{R_{\zeta,\delta\epsilon}(t,t_w)}{4B\ \psi_0(t_w)\ \psi_0(t)\ \left(1-\frac{\psi_0(t_w)^2}{2}\right)} \qquad (6)$$

For getting the integrated response function $\chi$, we apply the perturbation at different times after the quench. Then we measure in the experiment $R_{\zeta,\delta\epsilon}$ and the value of $\psi_0(t)$ as a function of time. These measured values are replaced in eq. 6 to compute $R(t,tw)$. The integrated response $\chi$ is obtained by a numerical integration of $R(t,t_w)$: $\chi(t,t_w) = \int_t^{t_w} R(t,t')\mathrm{d}t'$ The integrated response is related to the correlation by the FDR relations (see eq. 1). We study the FDR during an aging process by plotting the integrated response $\chi$ as a function of $C_\theta$. Due to the non-equilibrium process, it is not equivalent if the parameter is the waiting time $t_w$ or the observation time $t$.

First, $t_w$ is kept fixed. We can see in fig. 3 the FD plot for four typical values of the age of the system $t_w$. $\chi$ is a linear function of $C_\theta$ as stated by eq. 1 with a slope $1/T_{\mathrm{eff}}$ When $t_w$ increases, the slope $T_{\mathrm{eff}}$ tends to the temperature of the room $T$ as can be seen in fig. 3. The Fluctuation-Dissipation Theorem will be satisfied for large $t_w$. In the inset of figure 3, we have plotted the value of $T_{\mathrm{eff}}$ as a function of time $t_w$. We can see that $T_{\mathrm{eff}}$ decreases with $t_w$ and tends to the ambient temperature when $t_w$ tends to infinity.

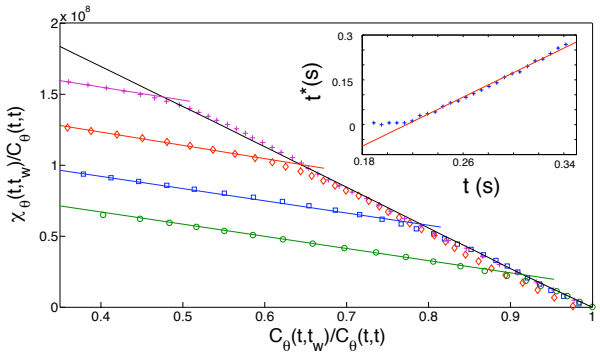



FIG. 4: a) Parametric plot integrated response versus correlation for $t = 0.4$ s ($\circ$), 0.5 s ($\Box$), 0.6 s ($\diamond$) and 0.7 s ($+$). Continuous line are linear fits. Dark line represents the FDT at equilibrium. Inset : the characteristic time $t^*$ is plotted as a function of $t$.

In a second time, $t$ is kept constant, which is the original way proposed by Cugliandolo and Kurchan and in theoretical papers on the aging at critical point [1, 7]. The FDR plots can be seen in figure 4 for four characteristics value of $t$. When $t_w$ is close to $t$ (when the correlation function is close to 1), the FDT is satisfied. Below a value, $C^*$, which depends on $t$, the Fluctuation Dissipation Theorem is not satisfied. The integrated linear response function remains linear in $C$ but the slope is almost three times the value at equilibrium. More precisely, if we define $t^*$ the characteristic time associated to the value of $C^*$. For $C < C^*$, $R$ remains linear in $C$ and the slope is not related to the thermal bath temperature $T$ but to a temperature $T_{eff}$, which is independent of $t$ and almost twice $T$. This means that the slow dynamics is characterized by a well defined temperature. In the inset of figure 4, we have plotted the value of $t^*$ as a function of $t$. We find that above a value of 0.22 s, $t^*$ is linear with $t$. The value 0.22 s corresponds to the relaxation time at the system at $\epsilon_0$. As simple picture can explained this observation : we separate the time scale between an aging part ($0 < t_w < 0.22$) and an equilibrium part ($t > 0.22$ s). $t^*$ is defined as the time between the equilibrium part and the aging one, thus it is equal to $t^* = t - 0.22$. This behavior matches very well the experimental result for $t > 0.22s$. The dependence of $T_{\rm eff}$ on the initial and final value of the quench is an important features which will be discussed in a longer report.

In conclusion we have shown that a LC quenched close to the critical point of the Fredericks transition presents aging features, such as a power law rescaling of correlation functions and the appearance of a well defined $T_{\rm eff} > T$ (working at fixed t). What is very interesting here is that although we are not exactly at $\epsilon = 0$ we observe a large interval of time where the predicted aging at critical point can be observed. The results plotted in fig.4 are not in perfect in agreement with those of ref. [7] for the mean field calculation of the aging at the critical point. The reason of this discrepancy is probably related to the fact that eq. 3 is an approximation for the dynamics of our system for which the spatial behavior cannot be neglected. This open the discussion for further theoretical and experimental development. Finally we want to stress that the results of fig.4 are in excellent quantitative agreement with the general predictions for the $T_{\rm eff}$ as defined by Cugliandolo and Kurchan. They show the existence of a very well define effective temperature independent of $t$ for the slow dynamics $t - t_w$ larger than a $t^*$. Notice that this result is in contrast with that of fig.3 where we see that the temperature is a decreasing function of $t_w$. This different behavior obtained by keeping fixed either $t$ or $t_w$ has been widely discussed in the theoretical literature, but it has never been so clearly observed in an experiment. This observation is actually very useful because in the study of FDR in polymers and colloids the procedure, which is often applied for several technical problem related to the measurement noise [3, 4] is the one with $t_w$ fix (fig.3). This of course may provoke several problems when comparing the experimental results with theory and our experimental results clearly point out this problem.

We acknowledge useful discussion with Peter Holdsworth. This work has been partially supported by ANR-05-BLAN-0105-01.

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