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To cite this version:

Sylvain Joubaud, Baptiste Percier, Artem Petrosyan, Sergio Ciliberto. Aging and effective temperatures near a critical point. 2009. ensl-00327521v2

HAL Id: ensl-00327521

https://ens-lyon.hal.science/ensl-00327521v2

Preprint submitted on 10 Feb 2009 (v2), last revised 6 Mar 2009 (v3)

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Aging and effective temperatures near a critical point

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(Dated: February 10, 2009)

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 several properties of an aging system after the quench, such as power law scaling in times 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. In this framework an important and general question which has been analyzed only theoretically is the relaxation of a system which is rapidly quenched exactly at the critical point of a second order phase transition [1, 2, 3, 4]. Because of the well known divergence of the relaxation time and of the correlation length the system presents a very rich dynamic, which has been named "aging at the critical point". Indeed this relaxation dynamic presents several properties which are reminiscent of those observed during the aging of spin glasses [1, 2, 3, 4, 5, 6] : the mean quantity has an algebraic decay and the correlation and response functions exhibit a power law scaling in time. Another important feature analyzed during the aging at a critical point concerns the equilibrium relation between response and correlation, *i.e.* the fluctuation dissipation theorem (FDT), which is not necessarily satisfied in an out of equilibrium system. This statement is relevant in the context of spin glass aging where a well defined (in the thermodynamic sense) effective temperature $T_{\rm eff}$ can be obtained using the so called fluctuation dissipation relation (FDR). This relation leads to the introduction of the fluctuation dissipation ratio, X, between correlation and response functions [5, 7]. Deviations of X from unity ($X = 1$ is the equilibrium value) may quantify the distance from equilibrium [7]. Equivalently an effective temperature $T_{\rm eff} = T/X$, larger than the heat bath temperature T, can be defined. Those ideas have been transferred to the aging at critical point, where for certain variables the FDR can be interpreted as a well defined effective temperature $T_{\rm eff}$ [1, 2].

The study of these analogies between the aging at the critical point and the aging of spin glasses is important because it allows to give new insight on the role of the quenched disorder on the above mentioned features and on the common mechanisms producing them. However these theoretical studies have been performed mainly on spin models and most importantly the reduced control parameter ϵ has been set exactly equal to zero. Thus one is interested to know how general these predictions are and also one may wonder whether those predictions can be observed in an experimental system where the exact condition $\epsilon = 0$ can never be reached.

The purpose of this letter is to analyze, within this theoretical framework, an experiment on the relaxation dynamic close to the critical point of a liquid crystal instability which is, at a first approximation, described by a Ginzburg-Landau equation and has the main features of a second order phase transition. The main result of our investigation is that after a quench close to the critical point the effective temperature $T_{\rm eff}$, measured from FDR, has a well defined value larger than the thermal bath temperature.

This kind of experimental test is important because the properties of X and $T_{\rm eff}$ have attracted much interest, since they suggest that a generalized statistical mechanics can be defined for a broad class of non equilibrium phenomena. Several theoretical models or numerical simulations show such a behavior [5, 8]. However in experiments the results are less clear and the relevance for real materials of the $T_{\rm eff}$ as defined by FDR is still an open question, which merits investigation [9, 10, 11, 12]. For example, there are important differences, which are not understood, between supercooled fluids [9], polymers[11], gels[10] and spin glasses[12]. The point is that on this subject it is very difficult to find simple theoretical models which can be directly compared with experiments. Thus the experimental study of the relaxation dynamics close to the critical point is very useful in this sense.

The system of our interest is the Fréedericksz transition of a liquid crystal (LC), subjected to an electric field $\vec{E}$ [13, 14]. In this system, we measure the variable ζ which is the spatially averaged alignment of the LC molecules, whose local direction of alignment is defined by the unit pseudo 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 $L = 9$ μm. 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 the x-axis[15]. The cell is next filled by a LC having a positive dielectric anisotropy (p-pentyl-cyanobiphenyl, 5CB, produced by Merck). The LC is subjected to an electric field perpendicular to the plates, by applying a voltage V between the ITO electrodes, *i.e.* $E = V/L$. To avoid the electrical polarization of the LC, we apply an AC voltage at a frequency $f_V = 1$ kHz ($V = \sqrt{2}V_0 \cos(2\pi f_V t)$) [13, 14]. More details on the experimental set-up can be found in ref.[16, 17]. 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 [13, 14]. For V_0 close to V_c the motion of the director is characterized by its angular displacement θ in xz-plane (θ is the angle between the x axis and $\vec{n}$), whose space-time dependence has the following form : $\theta = \theta_0(x, y, t) \sin\left(\frac{\pi z}{L}\right)$ [13, 14, 18]. If θ_0 remains small then its dynamics is described by a Ginzburg-Landau equation, which, neglecting the (x, y) dependence of θ_0,

$$\tau_0 \frac{\mathrm{d}\theta_0}{\mathrm{d}t} = \epsilon\, \theta_0 - \frac{1}{2}(\kappa + \epsilon + 1)\theta_0^3 + \eta \qquad (1)$$

where $\epsilon = \frac{V_0^2}{V_c^2} - 1$ is the reduced control parameter. The characteristic time τ_0 and constant k depend on the LC material properties. η is a thermal noise delta-correlated in time [18].

We define the variable ζ 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 θ_0 remains small, ζ takes a simple form in terms of θ_0 ($n_x = \cos(\theta)$) : $\zeta = 1/\mathcal{A} \iint_{\mathcal{A}} \mathrm{d}x\mathrm{d}y\theta_0^2$. It has been shown that ζ 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 [17, 20]. The measure of the variable ζ relies upon 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 measured using a polarization interferometer [19] which has a signal to noise ratio larger than 1000 (see ref. [16, 17] for details).

In this letter, we consider the dynamics of ζ 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 1 ms. As the typical relaxation time τ of ζ is about $10s$, at $\epsilon_0 \simeq 0$, this means that we can follow the out of equilibrium dynamics for about four orders of magnitude in time, which is really comparable to what is done in real glass experiments after a temperature quench where the dynamics is usually followed for about 3 or 4 decades in time. The advantage here is that 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 $< \cdot >$) of the measured quantities. We consider first the specific case of a quench from $\epsilon_1 = 0.3$ to $\epsilon_0 = 0.01$. The typical mean value $< \zeta(t) >$ of ζ 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 ζ is obtained by repeating the same quench 7000 times. The behavior of $< \zeta >$ remains constant for a certain time and then slowly relaxes (see fig. 1a). Above a characteristic time which is about 0.22 s in our case, the relaxation becomes exponential.

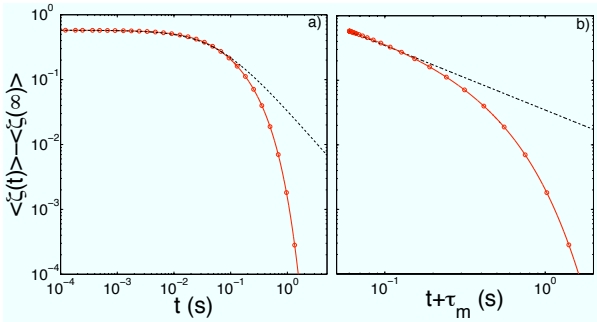

FIG. 1: a) Mean relaxation of the system, $\log\langle\zeta(t)\rangle$, as a function of time after a quench ($\circ$) from $\epsilon_1 = 0.3$ to $\epsilon_0 = 0.01$. The continuous line represents the theoretical response based on eq. 1 with $\langle\zeta\rangle \simeq \psi_0^2$. b) Mean relaxation of the system as a function of the reduced time $(t + \tau_m)$. in both figures the dashed lines represents the theoretical relaxation at $\epsilon = 0$.

To understand this behavior, we decompose the dynamics of θ_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 Ψ_0 obtained from the analytical solution of eq.1 is shown in fig.1 as a continuous line, which perfectly agrees with the measured dynamics. The experimental data and the solution of eq.1 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 $t \ll \tau \equiv \tau_0/(2\epsilon_0)$, the dynamics of ψ_0 is almost algebraic : $\psi_0(t) = \left[\frac{(\kappa+1)}{\tau_0}(t + \tau_m)\right]^{-1/2}$ with $\tau_m = \frac{\tau_0}{(\kappa+1)\psi_0(0)^2}$. This behavior, plotted in fig. 1 as a dashed line, is identical to the relaxation at the critical point [4]. Thus the system should present aging phenomena in the range $t < \tau$ which is the interval where the dashed line follows

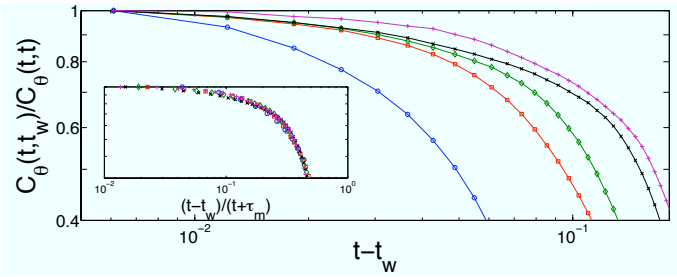

FIG. 2: a) Correlations functions $C_\theta(t,t_w)$ as a function of $t-t_w$ for different fixed $t=0.06$ s ($\circ$), 0.2 s ($\square$), 0.26 s ($\diamond$), 0.28 s ($\times$) and 0.31 s ($+$) after the same quench of fig. 1. Inset: The correlation functions have a simple master curve obtained by plotting $C_\theta(t,t_w)/C_\theta(t,t_w)$ versus $(t-t_w)/(t+\tau_m)$. Notice that $(t+\tau_m)$ is the reduced time used in fig.1

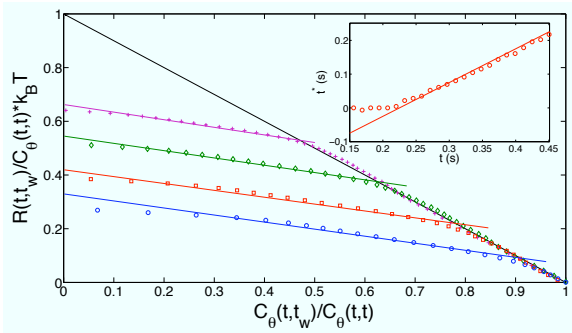

FIG. 3: a) Parametric plot integrated response versus correlation for $t=0.4$ s ($\circ$), 0.5 s ($\square$), 0.6 s ($\diamond$) and 0.7 s ($+$). Continuous line are linear fits. Dark line represents the FDT at equilibrium. Inset : the characteristic time t^* is plotted as a function of t.

the experimental data in fig. 1.

In order to measure $T_{\rm eff}$ as defined by the FDR, we need to measure both the correlation function $C_\theta(t,t_w) \equiv \langle\ \delta\theta_0(t)\ \delta\theta_0(t_w)\rangle$ of the thermal fluctuations $\delta\theta_0$ of θ_0 and the response function $\chi(t,t_w)$ of θ_0, at time t to a perturbation, given at time t_w, to its conjugated variable Γ, with $t_w < t$. More precisely, from ref.[5, 7] the effective temperature is:

$$\chi(t,t_w) = \frac{X(t,t_w)}{k_BT}[C_\theta(t,t) - C_\theta(t,t_w)] \qquad (3)$$

where k_B is the Boltzmann constant,T the heat bath temperature, i.e. $T_{\rm eff} = T/X(t,t_w)$.

To compute $\chi(t,t_w)$ and $C_\theta(t,t_w)$ in our experiment one has to consider that the measured variable is ζ. The relationship between the fluctuations of ζ and θ_0 has been discussed in details in ref.[16], thus we recall here only the useful results. As the area of the measuring beam is much larger than the correlation length, the global variable measured by the interferometer is $\zeta = \frac{1}{A}\iint \theta_0^2 {\rm d}x{\rm d}y \simeq \psi_0^2 + 2\psi_0\delta\theta_0$. Thus the mean value of ζ is $\langle\zeta(t)\rangle = \psi_0^2(t)$ and the fluctuations of $\delta\zeta$ of ζ can be related to the fluctuations of θ_0 : $\delta\zeta(t) = 2\psi_0(t)\delta\theta_0(t)$.

The autocorrelation function of θ_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 $(t-t_w)/(t+\tau_m)$. Thus in agreement with theoretical predictions, our system presents, during its slow relaxation after the quench close to the critical point, algebraic decay of mean quantities and the scaling of correlation functions which are very similar to the main features of spin glass aging (see for example [5, 6]).

The response function is obtained by applying a small change of the voltage V_0, which modifies the control parameter, *i.e.* $\epsilon = \epsilon_0 + \delta\epsilon$. In ref.[16] we have shown that the external torque Γ_{ext}, i.e. the conjugated variable of θ_0, associated to $\delta\epsilon$ is equal to :

$$\Gamma_{\rm ext} = 2B\ \delta\epsilon\ \psi_0(t)\ \left(1 - \frac{\psi_0(t)^2}{2}\right) \qquad (4)$$

We separate $\theta_0(t)$ into the average part $\psi_0(t)$, solution of eq. 1, with $\eta = 0$, and a deviation $\Delta(t)$ due to $\delta\epsilon$: $\theta_0(t) = \psi_0(t) + \Delta(t)$. We define the linear response function $R(t,t_w) =< \Delta > /\Gamma_{\rm ext}$ of θ_0 to Γ_{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 θ_0 to Γ_{ext} is:

$$R(t,t_w) = \frac{R_{\zeta,\delta\epsilon}(t,t_w)}{4B\ \psi_0(t_w)\ \psi_0(t)\ \left(1 - \frac{\psi_0(t_w)^2}{2}\right)} \qquad (5)$$

where $B = A\pi^2K_1/(4L)$, and K_1 a LC elastic constant. Thus inserting in eq.5 the measured values of $R_{\zeta,\delta\epsilon}(t,t_w)$, of $\psi_0(t)$ and of $\psi_0(t_w)$ we can measure $R(t,t_w)$ and by numerical integration we finally obtain $\chi(t,t_w) = \int_t^{t_w} R(t,t'){\rm d}t'$. The accuracy of this procedure has been checked at equilibrium in ref.[16] where we have shown that the measured C_{θ_0} and $\chi(t,t_w)$ verify FDT.

The integrated response is related to the correlation by the FDR relations (see eq. 3). Due to the non-equilibrium process, it is not equivalent if the parameter is the waiting time t_w or the observation time t (see ref.[8] for a detailed discussion on this point). Applying the correct procedure [2, 7], we keep the time t constant and we vary t_w, i.e. $0 < t_w < t$, and we repeat the procedure at various t. Following ref.[7], we study the FDR during the relaxation process by plotting the integrated response χ as a function of C_θ. These FDR plots can be seen in

fig. 3 for four characteristic values of t. When the system is in equilibrium the FDR plot is a straight line with slope $-1/(k_BT)$ (continuous line in fig. 3). The curves in fig. 3 for each t are composed by two straight lines and are remarkably similar to those predicted in theoretical models [7] and seen in experiments [12] of spin glasses aging. When t_w is close to t, i.e. large values of $C(t,t_w)$, the FDT is satisfied, i.e. the experimental points are on the continuous line in fig. 3. For $C(t,t_w)$ smaller than a value C^*, which depends on t, the FDT is not satisfied. However $\chi(t,t_w)$ remains linear in $C(t,t_w)$ but the slope, which does not depend on t, is much smaller than its value at equilibrium. This means that the slow modes of the systems have a very well defined temperature, independent of t, higher than that of the bath. Precisely we find, for $C(t,t_w) < C^*$, $X = T/T_{\text{eff}} = 0.31$, which is remarkably close to the asymptotic "universal" value $X = 0.34\pm0.02$ predicted for the small wave vector modes of an Ising model quenched at the critical point [2]. This analogy is important because our measurement, being an integral over the measuring volume, is more sensitive to the fluctuations coming from the long wavelength modes. In fig.3 we see that C^* is a decreasing function of t. Let us define t^* as the characteristic time associated with C^*. In the inset of fig. 3, we have plotted the value of t^* as a function of t. We find that $t^* \simeq 0$ for $t \leq \tau = 0.22s$. This indicates that, in agreement with ref.[2, 4], the violation occurs for all times at $\epsilon_0 = 0$. In our case it is cut by the exponential relaxation which starts at $t \simeq \tau$. For $t > \tau$, $t^* = t - \tau$ is linear in t, which also agrees with the theoretical picture of the FDR [7]. Indeed t^* separates the equilibrium part and the aging one and the ratio $t^*/t = 1 - \tau/t$, for $t > \tau$, defines how large is the equilibrium interval with respect to the total time. Notice that at $\epsilon_0 = 0$, $\tau = \infty$ and the equilibrium interval does not exist [2]. Thus the values of ϵ_0 and ϵ_1 affect only the amplitude of the region where the out of equilibrium is observed but not the value of X[21]. We also want to stress that this very clear scenario, with a well defined T_{eff} independent of t, is obtained only if the right procedure with fixed t is used [2, 8]. The results are completely different if t_w is kept fixed. In such a case T_{eff} is a decreasing function of t_w [21]. The non-commutability of the two procedures, i.e. either with t or with t_w fix, shows the non ergodicity of the phenomenon and opens a wide discussion on how to analyze the data in more complex situations, such as those where T_{eff} is measured in real materials and the procedure with t_w fixed is used [9, 10, 11, 12].

In conclusion we have shown that a LC quenched close to the critical point of the Fréedericksz transition presents aging features, such as a power law rescaling of correlation functions and the appearance of a well defined $T_{\text{eff}} > T$. Most importantly we show the existence of a well defined T_{eff} if the the right procedure with fixed t is used. What is very interesting here is that although we are not exactly at $\epsilon_0 = 0$ we observe a large interval of time,$0 < t < \tau$ where the predicted aging at critical point can be observed. The results plotted in fig.3 agree with those of ref. [2] but not with those of [4]. This means that the models of ref. [2] is certainly more adapted to describe our experimental systems. This opens the discussion for further theoretical and experimental developments. It also shows that the study of the quench at critical point is an interesting and not completely understood problem by itself [2, 4].

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

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