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# Intermittency of glassy relaxation and the emergence of a non-equilibrium spontaneous measure in the aging regime

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**Abstract.** – We consider heat exchange processes between non-equilibrium aging systems (in their activated regime) and the thermal bath in contact. We discuss a scenario where two different heat exchange processes concur in the overall heat dissipation: a stimulated fast process determined by the temperature of the bath and a spontaneous intermittent process determined by the fact that the system has been prepared in a non-equilibrium state. The latter is described by a probability distribution function (PDF) that has an exponential tail of width given by a parameter $\lambda$, and satisfies a fluctuation theorem (FT) governed by that parameter. The value of $\lambda$ is proportional to the so-called effective temperature, thereby providing a practical way to experimentally measure it by analyzing the PDF of intermittent events.

After decades of research many aspects of the glass state still defy our comprehension. Mode-coupling theory (MCT) provides a consistent framework [1] in the description of relaxational processes in a given temperature range. However, the structural arrest predicted by the ideal version of MCT is not observed, thereby activated processes have been advocated to drive the relaxation towards the equilibrium state. A physical description of these activated processes remains obscure as no clear experimental identification has been established. The presently accepted view is that activated processes are experimentally accessible through direct observation of cooperative motion of small (nanometer-sized) regions of particles, also called cooperatively rearranging regions (CRRs). Indirect evidences of activated processes have already been reported in confocal scanning microscopy [2,3] and light scattering [4] (using time-resolved correlation analysis) of colloidal systems. In addition, dielectric noise-sensitive measurements in glass formers have detected intermittent voltage signals with long tails in their corresponding probability distribution functions (PDFs) [5,6]. The purpose of this paper is to show that intermittency effects can be described in terms of a spontaneous (slow) heat exchange process between system and bath. Intermittency measurements provide a way to identify these spontaneous processes as well as to quantify violations of the fluctuation-dissipation theorem (FDT).

Let us consider a glass former quenched from a high temperature (where the system is initially equilibrated) to a lower value $T < T_{\rm MCT}$ ($T_{\rm MCT}$ being the MCT temperature) where slow relaxation and activated dynamics sets in. During the aging process heat $Q$ is constantly exchanged between the system and the bath. According to our view, this exchange occurs in two different ways that we will refer to as stimulated and spontaneous. The stimulated way corresponds to a continuous back-and-forth heat exchange between the sample and the bath, the net average heat exchange being zero on timescales much smaller than the age of the system $t_{\rm w}$. Were one to measure the statistical distribution $P^{\rm st}(Q)$ of the heat exchanged by this process between system and bath, along time intervals of a given duration, a Gaussian distribution centered around zero would be observed. We call this process stimulated because it is strictly dependent on the properties of the thermal bath meaning that the variance of $P^{\rm st}(Q)$ is dependent on $T$ but independent of $t_{\rm w}$. The spontaneous way of relaxation is different as it occurs in much longer timescales compared to the stimulated way and by an intermittent heat release from the system to the surroundings (and from there to the thermal bath), yet the net average of heat supplied by this mechanism is not zero. For, were one to measure the statistical distribution $P^{\rm sp}(Q)$ of the intermittent heat released to the bath by this process, an exponential tail characteristic of first-order Markov processes would be observed. This release of heat we call spontaneous because it is determined by the fact that the system has been prepared in a non-equilibrium state rather than by the value of the temperature $T$ of the bath. Therefore, in contrast to the previous case, the width of the exponential tail would be $T$-independent but $t_{\rm w}$-dependent and gradually change as the final equilibrium state is approached. During the aging process both heat exchange mechanisms concur, yet it would be possible to discern them by measuring the distribution $P(Q)$ of heat exchanged and disentangling the Gaussian and exponential components. We aim to validate the previous scenario by doing numerical simulations on a given class of models of glass-forming liquids and propose some predictions to be challenged in experiments.

To discern the stimulated and the spontaneous components, the following protocol has been implemented. Let us consider systems with stochastic dynamics. Initially, the system is equilibrated at a temperature $T_i \gg T_{\rm MCT}$. Then the temperature is instantaneously changed to $T < T_{\rm MCT}$ (this defines the initial time $t = 0$) and configurations evolved. In addition to the runtime configuration, it is convenient to keep track of the "valley" to which a given configuration belongs. A constructive approach to identify valleys has been proposed by Stillinger and Weber who have considered a topographic view of the potential energy landscape where valleys are called inherent structures (IS) [7]. The system is aged for a time $t_{\rm w}$ and the corresponding IS recorded. Dynamics goes on until a new IS is found, thereby defining the *first jump*. The exchanged heat $Q$ corresponding to that jump is recorded. For stochastic systems no work is exerted upon the system, so $Q = \Delta E = E(\mathcal{C}') - E(\mathcal{C})$, where $\mathcal{C}$ is the runtime configuration at $t_{\rm w}$ and $\mathcal{C}'$ the runtime configuration just after the first jump occurs. If $Q > 0$, then heat is transferred from the bath towards the system and vice versa. The quenching experiment is repeated many times, for each quench a value of $Q$ is obtained, and the probability distribution function (PDF) $P_{t_{\rm w}}(Q)$ is measured. Qualitative identical results are obtained if the runtime configuration is used to control the time when the first jump occurs. The main advantage of keeping track of the IS is that it provides a useful way to filter out collective spin (or particle) rearrangements. Related procedures have been used to analyze

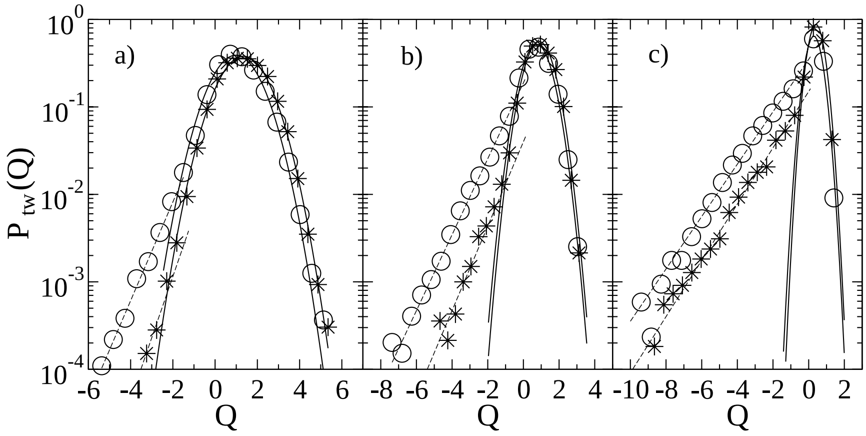

Fig. 1 – Heat exchange PDFs for a) $T = 0.3$, b) $T = 0.2$, c) $T = 0.1$. Circles are for $t_{\mathrm{w}} = 2^{10}$ and asterisks for $t_{\mathrm{w}} = 2^{15}$. The continuous lines are Gaussian fits to the stimulated sector, the dashed lines are the exponential fits to the spontaneous sector. The parameters of the fits are given in table I.

trapping time distributions [8–10]. Here we will concentrate our attention on the exchange heat distribution, establishing a link between the intermittency observed and the existence of a fluctuation theorem (FT) describing the spontaneous process.

We have considered the random-orthogonal spin-glass model (ROM) [11] which deserves interest as it is a good microscopic realization of the random-energy model, a phenomenological model of inherent simplicity commonly used in the study of disordered systems. Three different reasons motivate our choice: 1) The ROM is of the mean-field type (as interactions are long ranged) and shows dynamical properties in agreement with the predictions of the ideal version of MCT. It has been shown [11] to have a MCT transition temperature $T_{\mathrm{MCT}}$ below which the relaxation time diverges exponentially fast with $N$. 2) If $T < T_{\mathrm{MCT}}$ and the number of spins $N$ is finite, then activated processes are observable for long enough times [12]. Moreover, activation barriers can be tuned by changing the size of the system [13]. 3) Computation of $P_{t_{\mathrm{w}}}(Q)$ is numerically affordable. The ROM is defined in terms of a set of $N$ spin variables that can take two values $\sigma_i = \pm 1$, each configuration corresponding to a set of spin values, $\mathcal{C} = \{\sigma_i; 1 \le i \le N\}$. The energy $E$ of a configuration is given by $E = -2\sum_{i<j} J_{ij}\sigma_i\sigma_j$, where the $J_{ij}$ are Gaussian-distributed variables (zero mean and variance $1/N$) with correlations $\sum_{i=1}^{N} J_{ij}J_{ik} = \delta_{jk}$. A Monte Carlo dynamics is implemented where spins are randomly selected and updated, $\sigma_i \to -\sigma_i$ according to the Metropolis algorithm. For the sake of clarity, all along the paper, we will present results for $N = 64$ where the statistics collected is much better. Nevertheless, as a check of the correctness of our results, other sizes have been investigated $N = 32,\ 48,\ 300$ finding compatible results in all cases (the $N$-dependence of the values of the trapping times ensures that we are indeed observing activated processes). The ROM has a MCT transition temperature $T_{\mathrm{MCT}} \simeq 0.53$. Three quenching temperatures have been investigated $T = 0.3, 0.2, 0.1$ and around $10^4$ different quenches have been collected for each experiment. Figure 1 shows $P_{t_{\mathrm{w}}}(Q)$ for different values of $t_{\mathrm{w}}$ and $T$. It clearly shows the existence of two sectors, a Gaussian sector for small heat values of $Q$ and an exponential tail extending down to negative $Q$ values. The stimulated and the spontaneous sectors can be fitted to a Gaussian $P^{\mathrm{st}}_{t_{\mathrm{w}}}(Q) \sim \exp[-(Q-a)^2/(2b^2)]$ and an exponential function $P^{\mathrm{sp}}_{t_{\mathrm{w}}}(Q) \sim \exp[Q/\lambda]$, respectively. In general, there is no reason *a priori* for the spontaneous component not to

TABLE I – *Parameters for the Gaussian and exponential fits of fig.* 1.

| $T$ | 0.3 | | | 0.2 | | | 0.1 | | |
|---|---|---|---|---|---|---|---|---|---|
| $t_{\mathrm{w}}$ | $a$ | $b^2$ | $\lambda$ | $a$ | $b^2$ | $\lambda$ | $a$ | $b^2$ | $\lambda$ |
| $2^{10}$ | 0.98 | 1.03 | 0.77 | 0.75 | 0.50 | 1.00 | 0.29 | 0.17 | 1.45 |
| $2^{15}$ | 1.34 | 1.04 | 0.62 | 0.88 | 0.49 | 0.90 | 0.40 | 0.16 | 1.35 |

display a Gaussian correction, $P^{\mathrm{sp}}_{t_{\mathrm{w}}}(Q) \sim \exp[Q/\lambda + \mathcal{O}(Q^2)]$, yet for this particular example this correction appears negligible. In table I we show the results obtained for the fitting parameters. The numbers there reported confirm the scenario previously described. As the temperature of the bath decreases the width of the Gaussian $b^2$ decreases. On the other hand, the width of the Gaussian is nearly $t_{\mathrm{w}}$ independent and the width of the exponential tail $\lambda$ decreases with $t_{\mathrm{w}}$. Note that the average heat exchanged through the stimulated process (the parameter $a$) is different from zero, the reason being our protocol where values of $Q$ are measured along non-regularly spaced time intervals. In fact, only the average heat current (which has dimensions of energy divided by time) associated to the stimulated component vanishes. This is proportional to the heat exchanged only if heat exchange events are recorded at equal time intervals, which is not the case of our measurements.

The result for the spontaneous component $P^{\mathrm{sp}}_{t_{\mathrm{w}}}(Q) \propto \exp[Q/\lambda + \mathcal{O}(Q^2)]$ can be recast in the form of a FT [14],

$$\frac{P^{\mathrm{sp}}_{t_{\mathrm{w}}}(Q)}{P^{\mathrm{sp}}_{t_{\mathrm{w}}}(-Q)} = \exp\left[\frac{2Q}{\lambda}\right]. \tag{1}$$

An explicit numerical check of this identity requires to identify the spontaneous component $P^{\mathrm{sp}}_{t_{\mathrm{w}}}(Q)$ out of the global distribution $P_{t_{\mathrm{w}}}(Q)$. This is a difficult task, as heat fluctuations with $Q > 0$ are masked by the stimulated component. Actually, spontaneous events with $Q > 0$ are never observed; however they enter into the formulation of the FT as explicitly stated in (1). We have to remark that there is an important difference between (1) and the so-called conventional FTs. For the latter, transitions in both the forward and reverse directions are observed, while in the present aging case only spontaneous transitions with $Q < 0$ are observed. We plan to substantiate the fact that the easiest way to probe spontaneous transitions with $Q > 0$ is by applying an external perturbation that lifts the energy levels of the system making these transitions accessible. This is accomplished by the evaluation of fluctuation-dissipation relations as they specifically contain these transitions. A general feature of glassy systems is the existence of FDT violations [15] that have been interpreted in terms of an effective macroscopic temperature $T_{\mathrm{eff}}$ [16]. Previous considerations and the validity of (1) call for a connection between the value of $\lambda$ and the effective temperature $T_{\mathrm{eff}}$ as derived from the modified FDT. The proof is based on a microcanonical entropic argument *à la Edwards* used in granular media [17] that counts the number of valleys with free energy $F$ available to the system (for a discussion of how partitioning of the phase space in valleys can be accomplished see [15]). Let $\Omega(F)$ stand for the number of valleys of free energy $F$ and let $Q$ be the heat released to the system when jumping from a valley of free energy $F$ to a valley of free energy $F'$. Because spontaneous transitions are entropically driven, the distribution $P^{\mathrm{sp}}_{t_{\mathrm{w}}}(Q)$ is proportional to the number $\Omega(F')$. For the ratio between the forward and reverse transitions, we can write

$$\frac{P^{\mathrm{sp}}_{t_{\mathrm{w}}}(Q)}{P^{\mathrm{sp}}_{t_{\mathrm{w}}}(-Q)} = \frac{\Omega(F')}{\Omega(F)}\,. \tag{2}$$

The number of valleys with a given free energy defines a configurational entropy of valleys $S_{\mathrm{c}}(F) = \log(\Omega(F))$. Inserting this dependence and identifying (2) with (1), we obtain

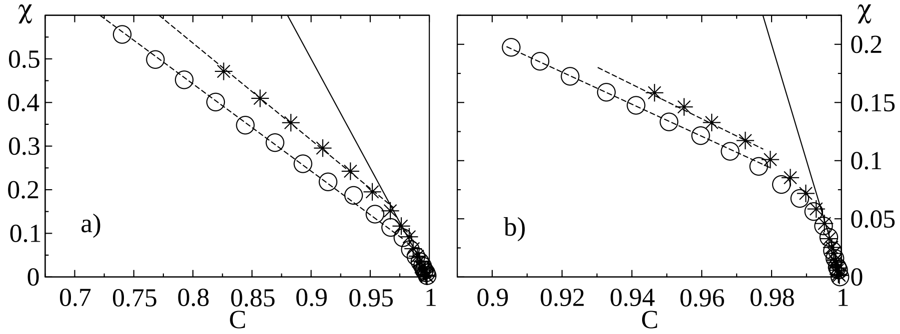

Fig. 2 – Fluctuation-dissipation plots for $T = 0.2$ (panel a)), $T = 0.1$ (panel b)) for $t_\mathrm{w} = 2^{10}$ (circles) and $t_\mathrm{w} = 2^{15}$ (asterisks). The intensity of the field is $h_0 = 0.1$. The continuous line is the equilibrium result $\chi(C) = (1 - C)/T$, the dashed lines are single parameter fits to the linear relation $\chi(C) = a - C/T_\mathrm{eff}$, where $a$ is the fit parameter and $T_\mathrm{eff} = \lambda/2$ is obtained from the values reported in table I.

$\exp[\frac{2Q}{\lambda}] = \exp[\frac{\partial S_\mathrm{c}(F)}{\partial F}\Delta F]$, where $\Delta F = F' - F$ and where we have kept the linear term in $\Delta F$ in the r.h.s. Using the relation $\Delta F = \Delta E - T\Delta S$ and the identity $Q = \Delta E$ as well as the definition for the effective temperature $1/T_\mathrm{eff} = \frac{\partial S_\mathrm{c}(F)}{\partial F}$, we obtain the result

$$\frac{1}{\lambda} = \frac{1}{2T_\mathrm{eff}}\left(1 - T\frac{\partial S(E)}{\partial E}\right), \tag{3}$$

where $S(E)$ denotes the dependence of the entropy of individual valleys on their average energy $E$. A good approximation amounts to retaining valleys as having very similar properties, in that case $S(E)$ is only a function of the temperature of the bath and $\lambda = 2T_\mathrm{eff}$. In other cases, however, $S(E)$ is simply very small and so is the term $\frac{\partial S(E)}{\partial E}$. This is the case of the ROM where, among other features, the entropy of valleys has been shown to be quite small [18], so the identity $\lambda = 2T_\mathrm{eff}$ is expected to be a good approximation. Let us mention that both $\lambda$ and $T_\mathrm{eff}$ in (3) are time dependent, a consequence of the existence of activated processes. The identity (3) is challenged in fig. 2, where we show the corresponding fluctuation-dissipation plots. These are constructed by evaluating the zero-field–cooled susceptibility $\chi(t, t_\mathrm{w})$ at time $t$ after applying a small field $h_0$ at $t_\mathrm{w}$, the corresponding two-times correlation $C(t, t_\mathrm{w})$, and plotting one in terms of the other [15]. The identity $\lambda = 2T_\mathrm{eff}$ is well verified in all cases.

To better justify the FT (1) and the identity (3), we have considered a family of exactly solvable models where these results can be explicitly checked. The family of models is defined by an ensemble of $N$ one-dimensional oscillators described by the variables $\{x_i; 1 \leq i \leq N\}$, where $-\infty < x_i \leq \infty$. Oscillators are subject to a potential $V(x) = \frac{k}{2p}x^{2p}$, where $k$ is a stiffness constant and $p$ is an integer $p \geq 1$. The total energy of the ensemble is given by $E = \sum_{i=1}^{N} V(x_i)$. For this family of models to show glassy behavior at low temperatures we consider a Monte Carlo dynamics where oscillator positions are updated in parallel $x_i \to x_i + \frac{r_i}{\sqrt{N}}$, and the $r_i$ are random distributed variables of zero mean and variance $\Delta^2$. The case $p = 1$ corresponds to the harmonic-oscillator model introduced in [19]. At $T = 0$, relaxation becomes logarithmic and the system partially equilibrates over the surface of constant energy with spontaneous energy decays whenever a configuration with lower energy is found. In such adiabatic regime, each configuration corresponds to a valley, so the identity $\lambda = 2T_\mathrm{eff}$ is expected to be exact. Moreover, at $T = 0$ there is no stimulated component, all heat exchanges are spontaneous and $P_{t_{\rm w}}(Q) = P^{\rm sp}_{t_{\rm w}}(Q)$. Analytical computations [20] show that (1) is exact with $\lambda = \frac{2kh_{2p}}{(2p-1)h_p}$ and $h_p = \langle x^{2(p-1)} \rangle$. For relaxation is adiabatic, the moments $h_p$, albeit time-dependent functions through the energy $E$, are related to each other by the corresponding equilibrium relations. A straightforward calculation gives $h_{2p}/h_p = (2p-1)(2p)E/Nk$. Inserting this expression into the previous one, we get $\lambda = 4pE/N$, and using the relation $S_{\rm c}(E) = \frac{N}{2p}\log(E)$, we obtain $\lambda = 2/S'_{\rm c}(E) = 2T_{\rm eff}$. As we said, the total entropy coincides with the configurational entropy as configurations correspond to valleys.

Albeit in a different context, a FT strikingly similar to (1) has recently been obtained [21] for the case of a Brownian particle in a steady state when dragged by a moving harmonic potential and subjected to a viscous drag force. The result (1) underlies the connection between intermittency and entropy production in the aging regime beyond the case of non-equilibrium systems in their steady states [22–24]. This raises the intriguing possibility that heat exchange FTs are widespread in condensed-matter physics in many non-equilibrium situations. An important aspect about why the intermittent effects here reported are numerically observable relies on the smallness of the simulated sizes. For larger sizes, exponential tails are less efficiently sampled and statistics must be larger to observe them. This fact might be relevant to our understanding of heat exchange processes in small systems driven out of equilibrium where energies are several times $k_{\rm B}T$, a problem of much current interest in nanoscience and biophysics as it might have potential implications for biology and life in general [25].

The experimental determination of the two types of heat emission here described could be addressed in Nyquist noise measurements of glass formers where voltage noise fluctuations induce heat dissipation in the resonant cavity. Indeed the heat dissipated by a resonant cavity of resistive impedance $Z(\omega)$ should be proportional to $V^2(\omega)/Z(\omega)$ and intermittent bursts in the voltage signal would correspond to spontaneously dissipated heat events. Actually, recent experiments [6] have obtained PDFs of the voltage signal $V$ whose profile is strikingly similar to the results shown in fig. 1. Moreover, these profiles show the presence of exponential tails whose width decrease in time (in agreement with our results) that we interpret in terms of a time-dependent effective temperature. Conversion of the voltage into dissipated power will result in a signal whose PDF still shows intermittency. The width of the exponential tail will satisfy $\lambda(t_{\rm w}) = cT_{\rm eff}(t_{\rm w})$, the structural constant $c$ depending on the cavity as well as on the type of coupling between the system and the cavity. In general, intermittency measurements offer a potentially interesting vein where new quantitative results on the non-equilibrium dynamics of slow systems can be inferred. Finally, let us mention that the existence of a FT that governs heat exchanges in the non-equilibrium aging state can be further investigated in numerical and theoretical investigations of other models for the glass transition. Our preliminary investigations in Lennard-Jones binary mixtures confirm the present results. These ideas could also be extended to granular systems where now relaxed free volume (instead of released heat) would govern the relaxation [26]. The results here purported suggest the existence of an interesting link between general theoretical aspects of the non-equilibrium dynamics of glass formers in their aging regime and intermittent noise signals experimentally measurable by different methods. Further work in experiments, theory and simulations will clarify the implications and potentialities of the present approach.

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