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 to describe relaxational processes experimentally observed 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 toward the equilibrium state. A physical description of these activated processes remains obscure as no clear experimental identification has been established. It has been long suspected that activated processes in glasses are not driven by free-energy differences between nucleating phases (e.g. liquid versus solid) but rather by an entropic mechanism involving decay among a large number of physically indistinguishable coexisting phases. This coexistence is a rather new concept in statistical physics, however it is one of the central elements in spin-glass theory, known to provide a good qualitative description of many aspects experimentally observed in disordered magnets and structural glasses. From the experimental point of view the identification of such activated processes appears challenging as no specific physical property can be targeted. 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 activation events have been already reported in confocal scanning microscopy and light scattering (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 the corresponding probability distribution functions (PDFs) [7, 8]. The purpose of this paper is to show that activated processes in structural glasses are related to intermittency effects theoretically described in terms of a spontaneous heat exchange process that generates a non-equilibrium measure and an associated fluctuation theorem (FT). Intermittency measurements provide a way to identify these spontaneous processes as well as quantify FDT violations.

Let us consider a glass former quenched from a high temperature (where the system is initially equilibrated) to a lower value $T < T_{\text{MCT}}$ ($T_{\text{MCT}}$ 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 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 $t_w$. Were one to measure the statistical distribution $P_{\text{st}}(Q)$ of the heat released by this process from system to bath along $N_t$ time intervals of regular duration $\Delta t$, a Gaussian distribution centered around zero would be observed. We call this process stimulated because it is strictly dependent on the presence of the thermal bath meaning that the variance of $P_{\text{st}}(Q)$ is dependent on $T$ but independent of $t_w$. The spontaneous way of relaxation is different as it occurs in a much longer timescale compared to the stimulated way. It occurs 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 $P_{\text{sp}}(Q)$ of the intermittent heat released from system 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 $t_w$ dependent and gradually change as the final equilibrium state is approached. During an aging process both heat exchange mechanisms appear intertwined in a complex pattern, yet it would be possible to discern them by measuring the distribution $P(Q)$ of heat exchanged and disentangling the Gaussian and exponential components. Unfortunately, the measurement of heat transfer between the system and the bath appears very difficult so one has to look for indirect ways of detecting the existence of these two processes. 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 from the global statistical distribution of transferred heat $P_{tw}(Q)$, the following protocol has been implemented (other choices lead to similar results, yet the the present one has revealed the most efficient). Let us consider systems with stochastic dynamics. Initially the system is equilibrated at a temperature $T_i \gg T_{\text{MCT}}$. Then the temperature is instantaneously changed to $T < T_{\text{MCT}}$ (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) [9]. The system is aged for a time $t_w$ and the corresponding IS recorded. Dynamics continues 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 $Q = \Delta E = E(C') - E(C)$ where $C$ is the runtime configuration at $t_w$ and $C'$ the runtime configuration just after the first jump occurs. If $Q > 0$ heat is transferred from the bath toward the system and vice versa.
The quenching experiment is repeated many times, each quench a value of \( Q \) is obtained, and the probability distribution function (PDF) \( P_{t_w}(Q) \) measured. Qualitative identical results are obtained if the runtime configuration is used to control 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 particles) rearrangements. Related procedures have been used to analyze trapping time distributions \[10\] \[11\] \[12\]. Here we will concentrate our attention in the exchange heat distribution, trying to establish a link between the intermittency observed and the existence of a FT describing the spontaneous process.

We have considered the random-orthogonal spin-glass model (ROM) \[13\] 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 \[8\]. 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 \[13\] to have a MCT transition temperature \( T_{MCT} \) below which the relaxation time diverges exponentially fast with \( N \); 2) If \( T < T_{MCT} \) and the number of spins \( N \) is not too large then activated processes are observable for long enough times \[13\]. Moreover, activation barriers can be tuned by changing the size of the system \[15\]; 3) Computation of \( P_{t_w}(Q) \) 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, \( C = \{ \sigma_i; 1 \leq i \leq N \} \). Spins interact via random exchange couplings \( J_{ij} \) leading to an energy function with strong disorder-induced frustration and therefore to a complex pattern of local minima. 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 \( \sigma_i \rightarrow -\sigma_i \) depending on the energy change \( \Delta E \) according to the Metropolis algorithm. For 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 identical results in all cases (the \( N \) dependence of the values of the trapping times ensure that we are indeed observing activated processes). The ROM has a MCT transition temperature \( T_{MCT} \approx 0.53 \). 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 \[11\] shows the \( P_{t_w}(Q) \) for different values of \( t_w \) 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. A salient feature of this figure is the clear cut distinction existing between the two sectors, the total amount of heat released by the spontaneous mechanism is generally quite small (compared to the overall absolute value of the heat exchanged through the stimulated process) yet the spontaneous decay is the leading mechanism by which heat is released to the bath. The stimulated and the spontaneous sectors can be very well fitted to a Gaussian \( P_{t_w}^{st}(Q) \sim \exp(-(Q-a)^2/(2\sigma^2)) \) and an exponential function \( P_{t_w}^{sp}(Q) \sim \exp(Q/\lambda) \) respectively, the normalization constant of these distributions being unimportant. In general there is no reason a priori for the spontaneous component not to display a Gaussian correction, \( P_{t_w}^{sp}(Q) \sim \exp((Q/\lambda) + \mathcal{O}(Q^2)) \), yet in the present case 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 \( t_w \) independent and the width of the exponential tail \( \lambda \) decreases with \( t_w \). 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.

The result for the spontaneous component \( P_{sp}^{tw}(Q) \propto \exp(Q/\lambda + O(Q^2)) \) can be recast in the form of a FT [16],

\[
\frac{P_{sp}^{tw}(Q)}{P_{sp}^{tw}(-Q)} = \exp\left(\frac{2Q}{\lambda}\right).
\]

(1)

An explicit numerical check of this identity requires to identify the spontaneous component \( P_{sp}^{tw}(Q) \) out of the global distribution \( P_{tw}^{tw}(Q) \). 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. 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 violations of the fluctuation-dissipation theorem (FDT) [17] that lead to a modified version of the theorem and have been interpreted in terms of an effective macroscopic temperature \( T_{eff} \) [18]. An important aspect of effective temperatures is that they are generally uncoupled to the temperature of the bath, their emergence thought to be related to the presence of an exponential density of states. Previous considerations and the validity of [11] call for a connection between the value of \( \lambda \) and the effective temperature \( T_{eff} \) as derived from the modified FDT. The outcome of all these considerations is that \( \lambda \approx 2T_{eff} \), the factor 2 being consequence of the validity of the FT [11]. The proof of this relation is based on the presence of an exponential tail of the heat released from system to bath and a microcanonical entropic argument a la Edwards used in granular media [19] 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 [17]). 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 \( P_{sp}^{tw}(Q) \) is proportional to the number \( \Omega(F') \). For the ratio between the forward and reverse transitions we can write,

\[
\frac{P_{sp}^{tw}(Q)}{P_{sp}^{tw}(-Q)} = \frac{\Omega(F')}{\Omega(F)}.
\]

(2)

The number of valleys with a given free energy defines a configurational entropy of valleys \( S_v(F) = \log(\Omega(F)) \). Inserting this dependence and identifying [2] with [11] we obtain,

\[
\exp\left(\frac{2Q}{\lambda}\right) = \exp\left(\frac{\partial S_v(F)}{\partial F} \Delta F\right).
\]

(3)

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

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

Table 1: Fit parameters for the Gaussian and exponential fits of Fig. [11]
Figure 1: Heat exchange PDFs for $T = 0.3$ (panel a), $T = 0.2$ (panel b), $T = 0.1$ (panel c). Circles are for $t_w = 2^{10}$ and asterisks for $t_w = 2^{15}$. 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 II.
Figure 2: Fluctuation-dissipation plots for $T = 0.2$ (panel a), $T = 0.1$ (panel b) and $t_w = 2^{10}$ (circles) and asterisks for $t_w = 2^{15}$ (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 $\chi(C) = a + C/T_{\text{eff}}$ where $a$ is the fit parameter and $T_{\text{eff}} = \lambda/2$ is obtained from the values reported in Table I.

In other cases, however, $S(E)$ is simply very small and so is the term $\partial S(E)/\partial E$. This is the case of the ROM where, among other features, the entropy of valleys has been shown to be quite small \(^{20}\) so the identity $\lambda = 2T_{\text{eff}}$ is a very good approximation. Let us mention that both $\lambda$ and $T_{\text{eff}}$ are time dependent, an indirect manifestation of the existence of activated processes. The identity \(^{4}\) is challenged in Figure 2 where we show the corresponding fluctuation-dissipation plots. These are constructed by evaluating the zero-field cooled susceptibility $\chi(t, t_w)$ at time $t$ after applying a small field $h_0$ at $t_w$, the corresponding correlation $C(t, t_w)$, and plotting one in terms of the other \(^{17}\). The identity $\lambda = 2T_{\text{eff}}$ is well verified in all cases.

To better justify the FT \(^{1}\) and the identity \(^{4}\) 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 $V(x) = k x^{2p}$ where $k$ is a stiffness constant and $p$ is an integer $p \geq 1$. The total energy of the ensemble is given by $E = \sum_{i=1}^{N} V(x_i)$. The model being non-interacting has no phase transition at finite temperature and the partition function is given by $Z = Z_1^N$ with $Z_1 = \int_{-\infty}^{\infty} dx \exp(-\beta V(x))$. 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 \( x_i \rightarrow x_i + \frac{r_i}{\sqrt{N}} \), 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 [21]. The Monte Carlo dynamics generates glassy behavior at \( T = 0 \) as the ground state configuration \( x_i = 0 \) has zero measure, thereby remaining unaccessible due to the finite value of the step distance \( \Delta \). 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 \( \lambda = 2T_{\text{eff}} \) is expected to be exact. Moreover because at \( T = 0 \) there is no stimulated component, all heat exchanges are spontaneous and \( P_{\text{sp}}(Q) = P_{\text{sp}}^{1,p}(Q) \). Rather than addressing the full dynamical solution [25] we content ourselves to present the main steps of the calculation. To compute the \( P_{\text{sp}}(Q) \) is enough to determine the PDF of energy changes given by \( \Delta E = Q = k \sum_i \sum_{l=1}^{2p} \left( \frac{2p}{i} \right) x_i^{2p-l} r_i N^{-1/2} \).

It is easy to verify that such a distribution is a Gaussian of mean \( \bar{Q} = \frac{k(p-1)}{2} \Delta^2 h_p \) and variance \( \bar{Q}^2 - \bar{Q}^2 = k^2 \Delta^2 h_{2p} \) with \( h_p = \langle x^{2(p-1)} \rangle \), the average taken over dynamical histories. Inserting the expression for the Gaussian in the FT [1] gives the exact result \( \lambda = \frac{2k^2 h_{2p}}{(2p-1) h_p} \). For relaxation is adiabatic, the moments \( h_{2p} / h_p = (2p-1)(2p) E / N k \). Inserting this expression into the previous one we get \( \lambda = 4p E / N \), and using the relation \( S_c(E) = \frac{1}{2T_{\text{eff}}} \log(E) \) we obtain \( \lambda = 2 / S_c(E) = 2T_{\text{eff}} \). 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 been recently 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 [11] underlies the connection between intermittency and entropy production in the aging regime beyond the case of non-equilibrium systems in their steady states [22, 23]. This raises the intriguing possibility that heat exchange FTs are widespread in condensed matter physics in many non-equilibrium situations.

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 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 [8] have obtained PDFs of the voltage signal \( V \) whose profile is strikingly similar to the results shown in Figure [1]. Moreover, these profiles show the presence of exponential tails with a slowly decaying width (therefore, 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 \( \lambda(t_w) = cT_{\text{eff}}(t_w) \), the structural constant \( c \) depending on the cavity as well as on the type of coupling between the system and the cavity. Similarly, the non-Gaussian tails observed by time resolved correlation analysis of intensity signals in colloidal glasses [6] could be interpreted in terms of exponential tails describing spontaneous events where heat is released to the bath due to the existence of CRRs. 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. Preliminary investigations in Lennard-Jones binary mixtures confirm all the results we have presented for the ROM. A detailed exposition of these results will be presented in the future. These ideas could
be also extended to granular systems where now relaxed free volume (instead of released heat) would describe 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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