Fluctuation Relation for Weakly Ergodic Aging Systems

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A fluctuation relation for aging systems is introduced and verified by extensive numerical simulations.
It is based on the hypothesis of partial equilibration over phase-space regions in a scenario of entropy-
driven relaxation. The relation provides a simple alternative method, amenable of experimental imple-
mentation, to measure replica symmetry breaking parameters in aging systems. The connection with the
effective temperatures obtained from the fluctuation-dissipation theorem is discussed.

Nonequilibrium systems are characterized by a net energy transfer (in the form of work, heat, or mass) to the environment. Aging systems pertain to the category of weakly ergodic nonequilibrium systems [1,2] exhibiting slow relaxational dynamics and strong history-dependent effects where the fluctuation-dissipation theorem (FDT) is violated [3–6]. This has led to the introduction of the concept of nonequilibrium or effective temperature [7]. Despite the insight gained from exactly solvable models and other conceptual attempts (e.g., Refs. [8,9]), we still lack a clear understanding of the general picture describing aging systems. In contrast to stationary systems, aging systems are described by two time scales: the waiting time t_w elapsed since the system was set in the nonequilibrium state and the time $t > t_w$ at which measurements are taken. A characterization of the full spectrum of fluctuations appears to be key for a satisfactory understanding of the aging state.

Over the past several years, several results about energy fluctuations in nonequilibrium states have been obtained under the heading of fluctuation theorems [10,11]. Fluctuation theorems take slightly different mathematical forms, depending on the specific nonequilibrium context [12,13]. However, all them share the same common feature: They relate the probabilities of absorbing and releasing a given amount of energy under nonequilibrium conditions and they are useful in small systems and short times where energy fluctuations can be directly measured, allowing us, for example, to extract the free energies of kinetic molecular states from irreversible pulling experiments [14].

In this Letter, we present a theoretical derivation of a fluctuation relation in aging systems. The aging fluctuation relation (AFR) is based on the hypothesis of partial equilibration in a scenario of entropy-driven slow relaxation. It can be written in terms of a phase-space contraction factor x that bears resemblance to the order parameter

$x(q)$ defined in the context of spin glasses [15]. The new relation is further supported by extensive numerical simulations. The existence of an AFR was already suggested in Refs. [16,17] and was recently hinted at in a quench experiment of a gelatin droplet that exhibits a sol-gel transition [18]. In that reference, heat distributions were measured and shown to satisfy a fluctuation relation for a system in contact with two baths at different temperatures. Yet, it remains unclear whether the same relation applies to other aging systems. In contrast, the new relation we are proposing should be generally valid in aging systems and is amenable to future experimental verification in noise measurements of glass formers, critical systems, and small systems (e.g., single molecules).

The AFR.—Consider a system quenched at time $t = 0$ from a high-temperature equilibrium state down to temperature T, where it ages, exhibiting slow relaxation and activated dynamics phenomena. Such an aging state is characterized by a low entropy-production rate and loss of time-translational invariance [19]. During the aging process, the system continuously exchanges energy with the bath, but some relaxational events result in larger than typical amounts of heat Q released to the bath, leading to a net positive entropy production $\langle \Delta S \rangle = \langle Q \rangle / T > 0$, where the brackets $\langle \cdots \rangle$ denote the average over dynamical histories.

To analyze the spectrum of heat or entropy-production fluctuations in the aging state, we consider the Bochkov-Kuzovlev work fluctuation relation, originally introduced as a generalization of the FDT [20]. After a time t_w, elapsed since the system was quenched, a constant external perturbation of strength h coupled to an observable A is applied to the system. This will cause a change in A during its subsequent evolution. The entropy production during the time interval $[t_w, t]$ ($t \geq t_w$) caused by the perturbation is equal to $\Delta S_{t_w, t} = Q_{t_w, t}/T = h[A(t) - A(t_w)]/T = h\Delta A_{t_w, t}/T$. This quantity has been termed exclusive work

in Ref. [21] and satisfies a fluctuation relation if the system is equilibrated at t_w (which is not the case here). $\Delta S_{t_w,t}$ is a fluctuating quantity, changing upon repetition of the same experiment. Moreover, in the aging regime, where relaxation dynamics is ruled by the complex topological structure of the phase space, made of many almost degenerate metastable states, $\Delta S_{t_w,t}$ displays a strong intermittent behavior. This means that, for fixed t_w and ΔS, the requirement $\Delta S_{t_w,t} = \Delta S$ defines a very broad interval of times t covering many well separated time scales. In such a context, a data analysis for fixed t_w and t may be ambiguous since it may mix up processes with different time scales, as noticed some years ago in the framework of turbulence [22,23]. To overcome this problem, we define $P_{t_w}(\Delta S)$ as the probability of observing the value $\Delta S_{t_w,t} = \Delta S$ after t_w.

In Ref. [16], a similar approach, based on the concept of inherent structure, was used. The idea was to look for $\Delta S_{t_w,t}$ associated with the first jump out of an inherent structure. While this definition could in principle be used in a numerical simulation, it is far less useful in a real experiment. In contrast, the one proposed here is well suited for real experiments.

Despite the fact that the perturbing field h favors positive values of $\Delta S_{t_w,t}$, trajectories with negative values can be observed as well. We argue that, for long enough t_w, the probability of observing positive and negative values of ΔS satisfies the following fluctuation relation (AFR):

$$\log\left[\frac{P_{t_w}(\Delta S)}{P_{t_w}(-\Delta S)}\right] = x_{t_w}\frac{\Delta S}{k_B}, \tag{1}$$

where k_B is the Boltzmann constant (equal to 1 in the following). If at t_w the system is in equilibrium, then $x_{t_w} = 1$ and Eq. (1) reduces to the Bochkov-Kuzovlev work fluctuation relation [20,21].

In aging systems, such as glasses, the FDT is not violated for times $t - t_w \lesssim t_w$ after switching on the perturbation. This is because the degrees of freedom whose characteristic relaxation times are sufficiently smaller than t_w have equilibrated. In the present context, this means that small enough energy transfers between the system and the bath occur in equilibrium, and hence $x_{t_w} \simeq 1$. This remains true as long as $|\Delta S|$ is smaller than a crossover value ΔS^*, which sets the scale of the typical minimum energy transfer in processes that involve non-equilibrated degrees of freedom. For $|\Delta S| > \Delta S^*$, non-equilibrium energy exchange processes responsible for slow relaxation come into play, and the equality $x_{t_w} = 1$ is violated. Not all degrees of freedom can contribute to the relaxation process, some of them being frozen at t_w, and hence $x_{t_w} < 1$. As the system ages, more degrees of freedom equilibrate at t_w, and hence ΔS^* increases with t_w. In the limit $t_w \gg t_{eq}$, where t_{eq} is the equilibration time, all degrees of freedom have equilibrated and x_{t_w} converges to 1 for all ΔS. We note that this may not be the case for

mean-field models where metastable states have an infinite lifetime.

To justify Eq. (1), we consider a system whose time evolution is ruled by the Langevin equation

$$\frac{d\varphi}{dt} = -\frac{\delta}{\delta\varphi}H(\varphi) + h + \xi, \tag{2}$$

where φ is an N-dimensional field, $\xi(t)$ a Gaussian white noise (thermal noise) of zero average and correlation $\langle\xi(t)\xi(t')\rangle = 2T\delta(t - t')$, $-\delta H(\varphi)/\delta\varphi$ the force arising from the conservative energy $H(\varphi)$, and h the constant external field coupled to the macroscopic observable $\psi_t = \sum_i\varphi_t^i$, where i denotes a site index. Fluctuation relations derive from the behavior of the probability $\mathcal{P}$ of a trajectory $\{\varphi_s\}_{s\in[t_w,t]}$ and its *reverse* $\{\tilde{\varphi}_s\}_{s\in[t_w,t]} \equiv \{\varphi_{t+t_w-s}\}_{s\in[t_w,t]}$. These can be easily computed using the path integral formalism (see, e.g., Ref. [24]):

$$e^{-\Delta S_{t_w,t}+\Delta S^{eq}}\mathcal{P}[\{\varphi_s\}_{s\in[t_w,t]}] = \mathcal{P}[\{\tilde{\varphi}_s\}_{s\in[t_w,t]}], \tag{3}$$

where $\Delta S_{t_w,t} = \beta h(\psi_t - \psi_{t_w})$ and $\Delta S^{eq} = \beta[H(\varphi_t) - H(\varphi_{t_w})] = -\ln[P^{eq}(\varphi_t)/P^{eq}(\varphi_{t_w})]$. The quantities in the exponent depend on the trajectory end points only; then, summing over all trajectories from φ_{t_w} at t_w to φ_t at time t and including normalized probability distributions $P_0(\varphi_{t_w})$ and $P_1(\tilde{\varphi}_{t_w}) = P_1(\varphi_t)$ for the initial and final states, we get

$$e^{-\Delta S_{tot}}P(\varphi_t, t|\varphi_{t_w}, t_w)P_0(\varphi_{t_w}) = P(\varphi_{t_w}, t|\varphi_t, t_w)P_1(\varphi_t), \tag{4}$$

where $P(\varphi_t, t|\varphi_{t_w}, t_w)$ and $P(\varphi_{t_w}, t|\varphi_t, t_w)$ are the conditional probabilities of the forward $\varphi_{t_w} \to \varphi_t$ and reverse $\varphi_t \to \varphi_{t_w}$ trajectories, respectively, and $\Delta S_{tot} = \Delta S_{t_w,t} - \Delta S^{eq} + \Delta S_b$, with $\Delta S_b = -\ln[P_1(\varphi_t)/P_0(\varphi_{t_w})]$. From this relation, the following identity follows:

$$P_{t_w,t}(-\Delta S) = \langle\delta(\Delta S_{t_w,t} - \Delta S)e^{-\Delta S_{tot}}\rangle_{t_w,t}, \tag{5}$$

where the average is over the forward process $\varphi_{t_w} \to \varphi_t$ with initial probability distribution $P_0(\varphi_{t_w})$.

After the quench, the system partially equilibrates inside independent phase-space regions (that we will call cages), from which it will escape only after a time $t - t_w \sim t_w$. Therefore, when $t - t_w \ll t_w$, the system is in (partial) equilibrium with the thermal bath, $P_0(\varphi) = P_1(\varphi) \propto P^{eq}(\varphi)$, so that $\Delta S^{eq} = \Delta S_b$, $\Delta S_{tot} = \Delta S_{t_w,t}$, and from (5) one gets Eq. (1) with $x_{t_w} = 1$.

To study the opposite limit $t - t_w \gg t_w$, where the system can access different cages, we observe that $\Delta S_{t_w,t}$ depends only on the macroscopic variables ψ_t and ψ_{t_w}; then, the average on the right-hand side of (5) can be done by partial classification, that is, by averaging first over all paths with given initial and final states and then over ψ_t and ψ_{t_w}:

$$P_{t_w,t}(-\Delta S) = \int d\psi_{t_w} \int d\psi_t \delta(\Delta S_{t_w,t} - \Delta S)$$
$$\times \langle e^{-\Delta S_{tot}} \rangle_{\psi_{t_w} t_w; \psi_t t}, \tag{6}$$

where $\langle \cdots \rangle_{\psi_{t_w} t_w; \psi_t t}$ denote dynamical averages restricted to those trajectories starting with ψ_{t_w} at t_w and ending with ψ_t at t. Assuming the system is partially equilibrated over cages, the probability $P(\varphi|\psi)$ of a state φ in a cage with fixed ψ is proportional to $P^{eq}(\varphi)$ times the probability of having ψ in a cage. Thus, $P(\varphi|\psi) \propto P^{eq}(\varphi) \times \Omega_{cage}(\psi)/\Omega_{t_w}(\psi)$, where $\Omega_{cage}(\psi)$ is the number of states with ψ inside the cage, divided by the total number $\Omega_{t_w}(\psi)$ of accessible states, not necessarily in the same cage, with ψ. Under the hypothesis of partial equilibrium, $S_{cage}(\psi) = \ln\Omega_{cage}(\psi)$ is the thermal equilibrium entropy in the cage. $\Omega_{t_w}(\psi)$ depends on system age, since the more we wait the more degrees of freedom relax. $S_{t_w}(\psi) = \ln\Omega_{t_w}(\psi)$ is then smaller than the full thermodynamic entropy and converges to it only for $t_w \gg t_{eq}$. Using this ansatz for the probability distribution function of the initial and final states and the relation $\partial S_{cage}(\psi)/\partial \psi = \beta h$ together with the analogous $\partial S_{t_w}(\psi)/\partial \psi = x_{t_w}\beta h$, corrected through the coefficient $x_{t_w} < 1$ to account for the frozen degrees of freedom, we have $\Delta S^{eq} - \Delta S_b = \beta h(\psi_t - \psi_{t_w}) - x_{t_w}\beta h(\psi_t - \psi_{t_w}) = (1 - x_{t_w})\Delta S_{t_w,t}$. Inserting this form into (6), the AFR (1) follows. The coefficient x_{t_w} measures the phase-space contraction due to frozen degrees of freedom at t_w. Clearly, $x_{t_w} \rightarrow 1$ as $t_w \gg t_{eq}$.

Numerical tests.—We have tested the AFR (1) through Monte Carlo simulations of several model systems, but we report results for only three of them. The system, initially prepared in a high-temperature equilibrium state, is instantaneously quenched to a temperature T below the freezing transition temperature. After t_w, a perturbation of small intensity, to ensure a good statistics for trajectories with $\Delta S < 0$, is applied, and the fluctuations $\Delta A_{t_w,t}$ of the conjugated variable A are recorded at fixed time intervals $t - t_w$. The maximum recording time t was taken much larger than t_w to ensure good statistics. The procedure was repeated several times, $P_{t_w}(\Delta S)$ calculated from data binning and Eq. (1) tested to extract the value of x_{t_w}. To compare it with the parameter $x = T/T_{eff}(t_w)$ obtained from the FDT, the fluctuation-dissipation (FD) plots in the time domain were also measured using the standard procedures [3]. Both x parameters [the one derived from the AFR, Eq. (1), and the one derived from FDT] asymptotically coincide under general assumptions; see Ref. [25].

The first model is the random orthogonal model (ROM) defined by the Hamiltonian [3]

$$\mathcal{H} = -\sum_{1 \leq i < j \leq N} J_{ij}\sigma_i\sigma_j, \tag{7}$$

where $\sigma_i = \pm 1$ are Ising spins and $J_{ij} = J_{ji}$ quenched Gaussian variables of zero mean and variance $1/N$

satisfying $\sum_k J_{ik}J_{kj} = 16\delta_{ij}$, with $J_{ii} = 0$. The system is perturbed by a uniform magnetic field of strength h conjugated to the total magnetization $M(t) = \sum_i \sigma_i(t)$.

This model describes structural glasses in the mode coupling theory (MCT) approximation and has a dynamical MCT transition at $T_d = 0.536$. Below T_d, the system is dynamically confined into one of the many (exponentially large in number) metastable states and cannot reach full equilibrium. The equilibrium transition occurs at the lower static (or Kauzmann) temperature $T_c = 0.25$. The low-temperature behavior of the model is described by a one-step replica symmetry breaking (1RSB) order parameter. The typical signature of this is a two-slope FD plot.

Figure 1 shows results for the ROM. Two regimes can be distinguished, $x_{t_w} = 1$ for $|\Delta S| < \Delta S^*$ and $x_{t_w} < 1$ for $|\Delta S| > \Delta S^*$ ($\Delta S^* \simeq 2$ for $t_w = 1024$). The values of x_{t_w} agree quite well with $x = T/T_{eff}$, extracted from the FD plot [inset (b)].

As a more realistic system, we have studied an 80:20 binary mixture of type A and B particles interacting via a Lennard-Jones pair potential:

$$V_{\alpha\beta}(r) = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^6\right], \tag{8}$$

where α, $\beta = A$, B, r is the distance between the two particles, and the parameters $\sigma_{\alpha\beta}$, $\epsilon_{\alpha\beta}$ stand for the effective diameters and well depths between species α, β. The parameters for length and energy measured in units of σ_{AA} and ϵ_{AA} are $\epsilon_{BB} = 0.5$, $\epsilon_{AB} = 1.5$, $\sigma_{BB} = 0.88$, and $\sigma_{AB} = 0.80$ and are taken to prevent crystallization [26]. With this choice, a system of reduced density $\rho = 1.2$
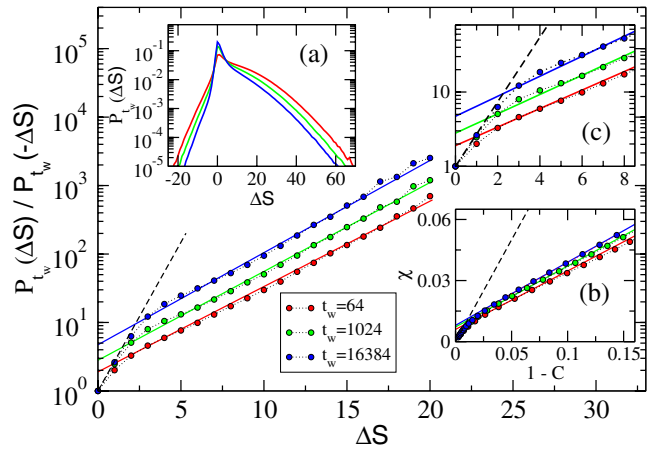

FIG. 1 (color online). Numerical test of the AFR in the ROM. The main plot is a test of Eq. (1) for the model with $N = 1000$, $T = 0.2$, and $h = 0.1$ at three values of t_w. The dashed line corresponds to $x_{t_w} = 1$ while the solid lines correspond to $x_{t_w} = 0.271$, 0.287, 0.299 for $t_w = 64, 1024, 16384$, respectively. (a) $P_{t_w}(\Delta S)$ and (b) FD plot. The dashed and solid lines shown in the FD plot have slopes equal to those shown in the main plot. (c) Zoom of the region corresponding to $x_{t_w} = 1$ (intracage relaxation).
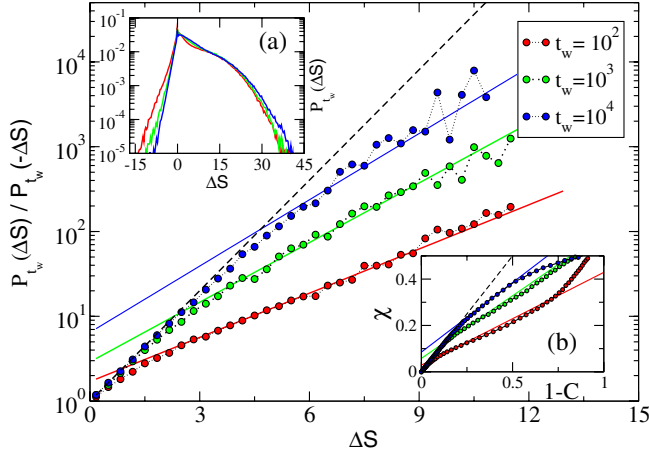
FIG. 2 (color online). Numerical test of the AFR in the binary mixture Lennard-Jones model. The main plot is a test of Eq. (1) for the model with parameters $N = 500$, $V_0 = 0.1$, $|k| = 7.25$, and $T = 0.3$ at three values of t_w. The dashed line corresponds to $x_{t_w} = 1$, while solid lines (bottom to top) correspond to $x_{t_w} = 0.40$, 0.54, 0.60 for $t_w = 10^2$, 10^3, 10^4, respectively. (a) $P_{t_w}(\Delta S)$ and (b) FD plot. The dashed and solid lines (bottom to top) in the FD plot have slopes equal to those shown in the main plot.
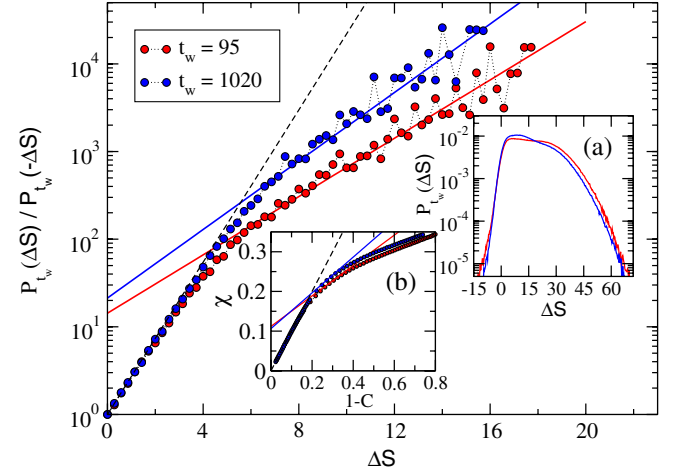

FIG. 3 (color online). Numerical test of the AFR in the 3D $\pm J$ EA model. The main plot is a test of Eq. (1) for the model with parameters $L = 16$, $T = 0.7$, and $h = 0.1$ at two values of t_w. The dashed line corresponds to $x_{t_w} = 1$, while solid lines (bottom to top) correspond to $x_{t_w} = 0.383$, 0.450 for $t_w = 95$, 1020, respectively. (a) $P_{t_w}(\Delta S)$ and (b) FD plot. The dashed and solid lines (bottom to top) in the FD plot have slopes equal to those shown in the main plot.

exhibits a glass transition well described by the MCT at the critical temperature $T_{\mathrm{MCT}} \simeq 0.435$. The study of the AFR was done by adding at time t_w an external potential of the form $V_0 \sum_j \epsilon_j \cos(\mathbf{k} \cdot \mathbf{r})$, where $V_0 < T$ and ϵ_j are independent identical distributed (quenched) random variables equal to ± 1 with equal probability, and by recording the conjugated observable $A_k(t) = \sum_j \epsilon_j \exp[i\mathbf{k} \cdot \mathbf{r}_j(t)]$ [27]. Results for the AFR are shown and compared with standard FD plots in Fig. 2. Also in this case, the agreement between the x extracted from the AFR and that from the FD plot is rather good. Interestingly, curves in the AFR plot do not exhibit the bending that can be seen in FD plots. Such bending is due to finite-size effects that for short t_w produce an equilibration of the system and a depletion of the statistics of rare events for longer t_w. The plot then bends upward for short t_w and downward for longer t_w.

Both of the above systems are described by a two-step relaxation, or 1RSB, scenario. As last example, we have considered the three-dimensional $\pm J$ Edwards-Anderson model ($\pm J$ EA) defined by the Hamiltonian (7), but with J_{ij} randomly chosen equal to ± 1 if the sites j and i are nearest neighbors on a cubic three-dimensional lattice and zero otherwise. Numerical investigation indicates that below $T \simeq 1.14$ there is a spin-glass phase described by a continuous-step relaxation, or full-RSB, scenario. The typical signature of this is a continuous-slope FD plot. Numerical tests of Eq. (1) for the $\pm J$ EA at two different t_w are shown in Fig. 3, together with the FD plot. The AFR is also well verified in this model. However, as shown in inset (b) and in contrast to the previous 1RSB models, the phase contraction coefficient x_{t_w} agrees

with T/T_{eff} only at the early stage, where the FD plot departs from equilibrium. This is in agreement with the aforementioned argument, according to which x_{t_w} gives information on the phase-space partition at t_w.

Discussion.—Summarizing, the AFR (1) shows a promising route to experimentally test the partial equilibrium-entropy-driven scenario in slowly relaxing systems from noise measurements. A theoretical derivation of the AFR was given and its validity verified by extended numerical experiments. The connection between the values of x_{t_w} extracted from the AFR and FD plots was shown. Remarkably enough, and in contrast to FD plots, extracting the value of x_{t_w} does not require measuring aging correlation functions. By only measuring the statistics of ΔS to an externally applied perturbation $P_{t_w}(\Delta S)$, we can test the validity of Eq. (1) to extract the value of x_{t_w}. We emphasize that, in order to test Eq. (1), statistical events with $\Delta S < 0$ must be observed. Since the average value of ΔS continuously increases with t, only rare events with $\Delta S < 0$ give full meaning to the AFR. A similar situation is encountered in the Gallavotti-Cohen theorem for steady state systems [28]. Equation (1) is ready to be employed in mesoscopic systems (e.g., magnetoconductance fluctuations in spin glasses and electron glasses [29,30]) and single molecule experiments. The latter include molecular systems exhibiting slow folding due to disorder and frustration (e.g., RNA) or slow binding kinetics (e.g., peptides or proteins binding DNA). Ultimately, small systems may provide direct access to experimentally measure the always elusive spin-glass order parameter.

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