Supplementary information of the paper

A fluctuation relation for weakly ergodic aging systems

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Contents

1. ABOUT THE CONNECTION BETWEEN THE AFR-X AND THE FD-X

We have argued that the parameter x_{t_w} appearing in Eq.1 (that we will call $x_{t_w}^{\rm AFR}$) is the same that appears in the Cugliandolo-Kurchan generalized fluctuation-dissipation relation (hereafter referred to as FDR) between correlations and responses (e.g. see Section 4.1 in Ref.[1]),

$$TR(t,t_w) = x_{t_w}^{\rm FD} \frac{\partial C(t,t_w)}{\partial t_w} \quad ; \tag{1}$$

where t_w is the waiting time, $t(> t_w)$ is a later time and $x_{t_w}^{\rm FD}$ stands for the fluctuation-dissipation parameter (herefater we take $k_B = 1$). The correlation C and response R appearing in Eq.(1) denote the so-called aging components of the correlation functions. Below we prove that, for $t, t_w, t/t_w$ large enough, and in a partial equilibration scenario, $x_{t_w}^{\rm AFR} = x_{t_w}^{\rm FD}$. The proof is split into two main parts: First we revisit the partial equilibration scenario and derive the equivalent of the AFR (Eq.1 in main text) using microcanonical arguments. Next we use the Onsager regression hypothesis to derive the extended fluctuation-dissipation relation and the equality $x_{t_w}^{\rm AFR} = x_{t_w}^{\rm FD}$. The following derivation is by no means a rigorous proof. It rather exposes the minimal elements of the physical picture potentially describing non-equilibrium relaxation in glassy systems. The equality between both x parameters has been proven in some exactly solvable models (e.g. in oscillator models [10]).

1.1. Microcanonical approach to derive of the AFR (Eq.1 in main text)

The significance of Eq.1 (main text) can be understood using a microcanonical approach based on a weak ergodicity scenario of partial equilibration [2]. The elements of such argument can be summarized as follows:

- **Partial equilibration.** After the quench, kinetics becomes slow enough at t_w for the system to partially equilibrate inside specific regions or components $\mathcal{R}$ of phase space. Phase space is then decomposed into disjoint partially-equilibrated regions (we say the phase space is partitioned). Each region may include one or more basins of attraction, e.g. defined in terms of inherent structures and often referred to as metabasins [3, 4]. The system attains partial equilibrium in a given region $\mathcal{R}$, meaning that configurations in that region, $\mathcal{C} \in \mathcal{R}$, are sampled according to restricted Boltzmann-Gibbs

conditional occupancies,

$$p_{t_w}(\mathcal{C}|\mathcal{R}) = \exp(-\beta(E(\mathcal{C}) - \mathcal{F}_{\mathcal{R}})) \tag{2}$$

where

$$\exp(-\beta\mathcal{F}_{\mathcal{R}}) = \sum_{\mathcal{C}} \exp(-\beta E(\mathcal{C})) \tag{3}$$

defines the (partial) free energy of region $\mathcal{R}$, $E(\mathcal{C})$ is the configurational energy and $\beta = 1/T$ with T the bath temperature.

- **Equal-probability postulate**. At a given time t_w after the quench, relaxational dynamics generates a partition of phase-space into regions, each region having a partial free energy according to eq.(3). We postulate that regions with identical partial free energy $\mathcal{F}_{\mathcal{R}}$ are uniformly sampled upon infinite repetitions of a quenching experiment. Yet partitioning of phase space into regions is t_w-dependent meaning that any region $\mathcal{R}$ will have different probabilities at different waiting times. In essence, this is the origin of the two-times dependence so characteristic of correlation functions during the aging process. As t_w increases, regions expand (in phase-space volume) and their total number decreases until eventually full equilibrium is attained over a single region englobing all phase space. This holds in a weak-ergodicity breaking scenario, e.g. for finite-size systems and $t_w \to \infty$. The details of the above scenario, e.g. how phase space partitioning changes with time, cannot be predicted unless equations of motion are solved (analytically or numerically) and the time evolution of the configurational probability distribution determined. How to do this starting from first principles remains presently unclear although there exist several proposals (e.g. based on the concept of inherent structures [5–8]).

The equal-probability postulate tells us that we can apply maximum entropy (i.e. maximum likelihood) arguments to determine how the system will evolve in response to an external perturbation. Let $\Omega(\mathcal{F}, \mathcal{A})$ be equal to the density of regions with free energy $\mathcal{F}$ and value $\mathcal{A}$ of a given observable $A(\mathcal{C})$,

$$\Omega(\mathcal{F}, \mathcal{A}) = \sum_{\mathcal{R}} \delta(\mathcal{F} - \mathcal{F}_{\mathcal{R}})\delta(\mathcal{A} - \mathcal{A}_{\mathcal{R}}) \tag{4}$$

with

$$\mathcal{A}_R = \sum_{\mathcal{C}} A(\mathcal{C}) p_{t_w}(\mathcal{C}|\mathcal{R}) \quad , \tag{5}$$

and $p_{t_w}(\mathcal{C}|\mathcal{R})$ being given in Eq.(2).

If a small field h coupled to A is applied at t_w, free energy of regions are shifted (to linear order in h) by $\mathcal{F}^h_\mathcal{R} = \mathcal{F}_\mathcal{R} - h\mathcal{A}_\mathcal{R}$, and the density of regions changes to

$$\Omega_h(\mathcal{F},\mathcal{A}) = \sum_\mathcal{R} \delta(\mathcal{F}-\mathcal{F}^h_\mathcal{R})\delta(\mathcal{A}-\mathcal{A}^h_\mathcal{R}) = \sum_\mathcal{R} \delta(\mathcal{F}-\mathcal{F}_\mathcal{R}+h\mathcal{A}_\mathcal{R})\delta(\mathcal{A}-\mathcal{A}_\mathcal{R}) = \Omega(\mathcal{F}+h\mathcal{A},\mathcal{A}) \tag{6}$$

This expression is valid only to linear order in h when $\beta h\mathcal{A} << 1$. Notice also that we took $\mathcal{A}^h_\mathcal{R} = \mathcal{A}_\mathcal{R}$ (i.e., the field does not change the values of $\mathcal{A}_\mathcal{R}$) to linear order in h, meaning that the field does neither *speed up* or *slow down* the relaxation process, keeping the partitioning of phase space unchanged. In other words, the field does not modify the trapping times of different regions to linear order in h. The applicability of these assumptions is dependent on the observable A. Those that satisfy such requirements are called *neutral* observables [9, 10] (see also Sec.4.4 in [1]). Non-neutral observables are behind several non-monotonic relaxation effects observed in structural glassses such as the Kovacs effect.

Small h now guarantees that the partitioning of phase space for $t > t_w$ remains unchanged with respect to $h = 0$. The postulate of equal-probability of regions gives $P_{t_w,t}(\mathcal{A}\to\mathcal{A}') \propto \Omega_h(\mathcal{F},\mathcal{A}')$ where $\mathcal{F}$ is the typical free energy of a region visited at t_w. Therefore,

$$\frac{P_{t_w,t}(\Delta\mathcal{A})}{P_{t_w,t}(-\Delta\mathcal{A})} = \frac{\Omega_h(\mathcal{F},\mathcal{A}')}{\Omega_h(\mathcal{F},\mathcal{A})} = \frac{\Omega(\mathcal{F}+h\mathcal{A}',\mathcal{A}')}{\Omega(\mathcal{F}+h\mathcal{A},\mathcal{A})} = \frac{\Omega(\mathcal{F},\mathcal{A}')}{\Omega(\mathcal{F},\mathcal{A})}\exp(\beta x_{t_w} h\Delta\mathcal{A}) = \exp(\beta x_{t_w} h\Delta\mathcal{A}) \tag{7}$$

with $\Delta\mathcal{A} = \mathcal{A}' - \mathcal{A}$ and

$$x^{\rm AFR}_{t_w} = T\Big(\frac{\partial\mathcal{S}_c}{\partial\mathcal{F}}\Big) \quad \text{with} \quad \mathcal{S}_c(\mathcal{F},\mathcal{A}) = \log(\Omega(\mathcal{F},\mathcal{A})) \quad , \tag{8}$$

where we used Eq.(6). In Eq.(8) $\mathcal{S}_c$ stands for the so-called configurational entropy or complexity and the partial derivative is taken at typical values ($\mathcal{F}$,$\mathcal{A}$) of regions visited at t_w. Note that in Eq.(7) we took $\Omega(\mathcal{F},\mathcal{A}') = \Omega(\mathcal{F},\mathcal{A})$ meaning that $(\frac{\partial\mathcal{S}_c}{\partial\mathcal{A}}) = 0$. This implies $P_{t_w,t}(\Delta\mathcal{A}) = P_{t_w,t}(-\Delta\mathcal{A})$ for $h = 0$, i.e. $\mathcal{A}$ is a neutral observable [9, 10]. Equation (7) with $\Delta S = \beta h\Delta\mathcal{A}$ gives the AFR, Eq.1 in main text, in the time sector $t >> t_w$ where net entropy production is contributed by inter-region relaxation.

1.2. Relation to the FD-x parameter.

Here we show that the parameter $x_{t_w}^{\rm AFR}$ defined in Eq.(8) is equal to the fluctuation-dissipation ratio $x_{t_w}^{\rm FD}$ that appears in the fluctuation-dissipation relation Eq.(1).

If a small field h coupled to A is applied at t_w the expectation value of the observable at a later time t is given by,

$$\langle A(t)\rangle = \sum_{\mathcal{R},\mathcal{R}'} \mathcal{A}_{\mathcal{R}} p_h(\mathcal{R},t|\mathcal{R}',t_w) P_{t_w}(\mathcal{R}') \tag{9}$$

where $p_h(\mathcal{R},t|\mathcal{R}',t_w)$ is the probability of the system to be in region $\mathcal{R}$ at time t conditioned to be in region $\mathcal{R}'$ at the previous time t_w in the presence of an applied (stepwise) field h at t_w; and $P_{t_w}(\mathcal{R}')$ is the (unperturbed, i.e. h=0) probability to be in region $\mathcal{R}'$ at time t_w during the quenching. According to Eq.(7), the transition probabilities $p_h(\mathcal{R},t|\mathcal{R}',t_w)$ in a field h satisfy

$$p_h(\mathcal{R},t|\mathcal{R}',t_w) = p_0(\mathcal{R},t|\mathcal{R}',t_w)\exp\Big(\beta x_{t_w} h(\mathcal{A}_{\mathcal{R}} - \mathcal{A}_{\mathcal{R}'})\Big) \tag{10}$$

where the region-dependent observables $\mathcal{A}_{\mathcal{R}}$ are defined in Eq.(5). Inserting Eq.(10) into Eq.(9) and expanding the exponential to linear oder in h we get,

$$\langle A(t)\rangle - \langle A(t)\rangle_0 = \beta x_{t_w} h \sum_{\mathcal{R},\mathcal{R}'} \mathcal{A}_{\mathcal{R}}(\mathcal{A}_{\mathcal{R}} - \mathcal{A}_{\mathcal{R}'}) p_0(\mathcal{R},t|\mathcal{R}',t_w) P_{t_w}(\mathcal{R}') = \beta x_{t_w} h\Big(\langle A^2(t)\rangle - \langle A(t)A(t_w)\rangle\Big) \quad . \tag{11}$$

If we know define the two-times correlation and response functions as,

$$C(t,s) = \langle A(t)A(s)\rangle \tag{12}$$

$$R(t,s) = \frac{\delta\langle A(t)\rangle}{\delta h(s)} \tag{13}$$

we then have,

$$\int_{t_w}^{t} R(t,s)ds = \lim_{h\to 0}\frac{\langle A(t)\rangle - \langle A(t)\rangle_0}{h} = \beta x_{t_w}\Big(C(t,t) - C(t,t_w)\Big) = \beta x_{t_w}\int_{t_w}^{t}\frac{\partial C(t,s)}{\partial s}ds \tag{14}$$

where we used Eqs.(11,12,13). Identifying the integrands at the beginning and end in Eq.(14) we get the FDT result Eq.(1) and the equality $x_{t_w}^{\rm AFR} = x_{t_w}^{\rm FD}$.

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