

Generalized Fluctuation-Dissipation Relation and Effective Temperature Upon Heating a Deeply Supercooled Liquid

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We show that a generalized fluctuation-dissipation relation applies upon instantaneously increasing the temperature of a deeply supercooled liquid. This has the same two-step shape of the relation found upon cooling the liquid, but with opposite violation, indicating an effective temperature that is lower than bath temperature. We show that the effective temperature exhibits some sensible time dependence and that it retains its connection with the partitioned phase space visited in aging. We underline the potential relevance of our numerical results for experimental studies of the fluctuation-dissipation relation in glassy systems.

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Introduction.—Supercooled liquids fall out of equilibrium almost inevitably. Indeed almost any liquid can be taken to some low-enough temperature (avoiding crystallization) where the structural relaxation processes become extremely slow and the cooling happens to be too quick for the system to equilibrate [1,2]. In this case we observe that the system slowly tries to adapt to the new temperature and exhibits time-dependent thermodynamic properties such as energy or pressure, entering a regime called physical aging. In such an off-equilibrium situation the correlation and the response functions characterizing the dynamics of the liquid lose time-translational symmetry, and the fluctuation-dissipation theorem (FDT) relating the two functions is not supposed to hold anymore [3,4].

However the interesting fact about glassy systems is that a general fluctuation-dissipation relation (FDR) seems to apply when they fall out of equilibrium [5–9]. The FDR allows us to rigorously define a time-dependent effective temperature that is found to reflect the separation of time scales occurring in the relaxation. In fact the analytic solution of schematic models [5,8,10,11], numerical simulations of realistic models of glassy systems [12–16], and few experimental evidences [17–20] suggest that when the system is rapidly cooled (quenched) to a low-enough bath temperature T_{bath} , the FDR may be written as follows:

$$T_{\text{bath}} \partial_{t'} \chi(t, t') = -X(t, t') \partial_{t'} C(t, t'). \quad (1)$$

In Eq. (1) $C(t, t') = \langle A(t)B(t') \rangle$ is the correlation function of the observables A and B and $\chi(t, t') = \langle A(t) \rangle / \epsilon_{\epsilon \rightarrow 0}$ is the response function to an external perturbation ϵ applied at the time t' and coupled to the system with an energy contribution $-\epsilon B$. $X(t, t')$ on the right-hand side of Eq. (1) is called violation factor and it allows one to introduce a time-dependent effective temperature $T_{\text{eff}}(t, t') = T_{\text{bath}}/X(t, t')$. Note that $X = 1$ at short time scales [i.e., $(t - t')/t' \ll 1$] where the FDR of Eq. (1) reduces to the FDT indicating that the fast “vibrational” dynamics of molecules is immediately equilibrated at the

bath temperature ($T_{\text{eff}} = T_{\text{bath}}$). Differently at long time scales [i.e., $(t - t')/t' \gg 1$] it is found that $X < 1$ suggesting that the slow structural dynamical rearrangements behave as if they were in equilibrium at a temperature $T_{\text{eff}} = T_{\text{bath}}/X$ higher than T_{bath} . This is a well-established scenario confirmed theoretically and numerically in the case where the system is taken out of equilibrium by rapidly cooling it down to the glassy phase. Nevertheless slow dynamics and aging effects can be observed in a glassy system without necessarily cooling it. It is possible, for example, to increase rapidly the temperature of an equilibrated supercooled liquid or a glass and obtain typical aging effects [21,22]. In this case it is interesting to ask what happens to the FDR and the associated T_{eff} since so far no study of this kind has been reported in the literature [23].

In this work we show, for the first time, that the FDR and the effective temperature concept can be extended to the case where an initially equilibrated deeply supercooled liquid is taken off equilibrium by suddenly heating it and letting it age towards a new equilibrium state. We find that the FDR displays the two slopes observed in quenches but with $X > 1$ at large time scales. This suggests that the slow dynamics behaves as if it were equilibrated at some T_{eff} that is lower than T_{bath} . Moreover we find that T_{eff} exhibits a strong dependence on the time elapsed from the instantaneous heating. Finally we show that the connection between T_{eff} and the potential energy landscape found in some glassy systems is conserved when the same systems are quickly heated. As argued in the following our results suggest a new route to test experimentally the breakdown of the FDT and measure T_{eff} .

Simulation.—We simulate a binary mixture (80:20) of 1000 particles interacting via the Kob-Andersen Lennard-Jones potential [25,26]. Equilibrium low-temperature configurations are produced by numerically integrating thermostatted Newtonian dynamics in the canonical ensemble for times of the order of 10^8 molecular dynamics

(MD) steps for the lowest T investigated [27]. MD simulations are run on high-end graphics processing units (GPUs) [28] that allow for a considerable speed up of the simulation that typically runs ~ 20 times faster on GPUs than on standard processors. Using such a massively parallel computing approach we produce from 5×10^3 to more than 10^4 independent initial configurations for each low-temperature state from which we perform our numerical heating experiments. The lowest temperature equilibrated is $T = 0.41$ at density $\rho = 1.2$, where the mode-coupling temperature is $T_{\text{MCT}} = 0.435$ [29]. To check that, for such low T , a genuine equilibrium state is obtained, we verify that the mean square displacement becomes diffusive and the correlation function (defined in the following) is fully decayed at long times. Moreover we check that the equilibration time is long enough that all particles have moved at least one particle diameter. For each low- T configuration we follow the off-equilibrium dynamics after an instantaneous temperature increase (T up jump) using the standard Monte Carlo (MC) Metropolis [30] algorithm in the canonical ensemble. The choice of MC dynamics allows us to employ a zero-field algorithm that can be used for obtaining the integrated response function without actually applying any external perturbation. With this technique, introduced in Ref. [16], the response is guaranteed to be free of any nonlinear contribution. Moreover this method provides the response as a function of t' (i.e., the instant at which the perturbation is applied) avoiding running one simulation for each t' .

Results.—We study the FDR and T_{eff} by building the parametric FD plot reporting $T_{\text{bath}}\chi(t, t')$ versus $C(t, t')$. In this way the FDT violation can be immediately visualized and estimated from the parametric curve, being $X = T_{\text{bath}}/T_{\text{eff}} = -T_{\text{bath}}\partial\chi(t, t')/\partial C(t, t')$ at large time scales. The variables A and B , defining χ and C , are chosen to be $A_{\mathbf{k}}(t) = N^{-1}\sum_j \eta_j \exp(i\mathbf{k} \cdot \mathbf{r}_j(t))$ and $B_{\mathbf{k}}(t) = N[A_{\mathbf{k}}(t) + A_{-\mathbf{k}}(t)]$, where the sum is extended to all N particles of the system with instantaneous positions $(\mathbf{r}_1(t), \dots, \mathbf{r}_N(t))$, and η_j is a bimodal random variable with zero mean. With this choice the correlation function coincides with the self-intermediate scattering function at wave vector \mathbf{k} .

Figure 1 shows that an evident FDT violation occurs when T_{bath} is instantaneously increased from a very low T . The time scales and the aging times studied here are of the same order of those studied in the quenches [15]; in Fig. 1 the time t' varies between 6×10^2 and $t = 8 \times 10^3$ MC steps where the time origin is set to the time at which the T up jump is performed. Note that the FD plot displays the two slopes already found in quenches, but with opposite violation. By looking at Fig. 1 it is also clear that the violation gradually disappears on increasing the final T . This is because the relaxation becomes so fast that it is not possible to see clearly, neither characterize, a regime where $X \neq 1$ in the FD plot. Differently, if the final T in the up jump is too close to the initial T , a very slow relaxation is

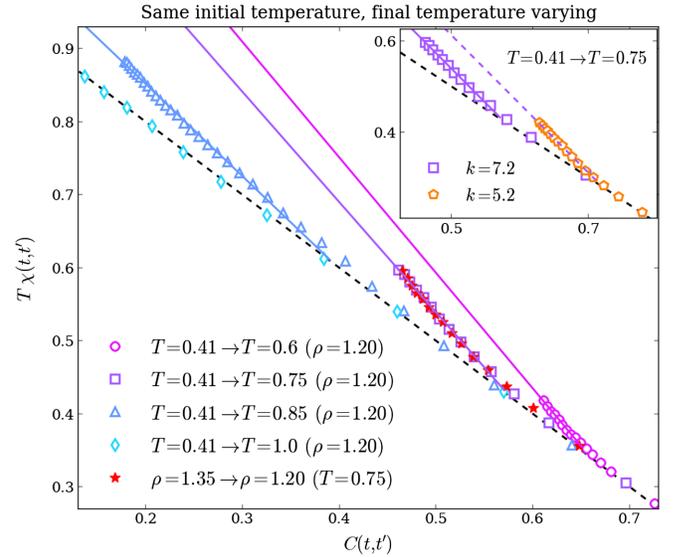


FIG. 1 (color online). Response versus correlation parametric plots (FD plots) for several temperature up jumps as the final (bath) temperature T_{bath} is varied. The time t' varies between 6×10^2 and $t = 8 \times 10^3$ MC steps. A violation of the FDT (dashed line) characterized by $X > 1$ (i.e., $T_{\text{eff}} < T$) is clearly observed at large time lags $t - t'$ as evidenced by the straight-line fits of the points departing from the FDT. It can be seen how, increasing the final temperature of the jump, the FDT violation is gradually lost. We show also how two identical FD plots can be generated by instantaneously increasing the volume (at fixed T) or the temperature (at fixed ρ) in analogy with the findings of Ref. [15]. Inset: FD plot in T up jump for two different wave vectors. The fitting line of the $k = 5.2$ case fits very well also the $k = 7.2$ case indicating that T_{eff} does not depend on the chosen wave vector as found also in quenches [13].

observed which is not suitable for our study. The inset of Fig. 1 shows that X does not depend on the wave vector \mathbf{k} entering in the definition of the correlation and the response, as observed in the case of quenches [13]. Moreover we verify that identical FD plots are obtained if we increase T or if we decrease ρ instantaneously starting from initial states that are connected by the density-scaling equation [31] (Fig. 1). This confirms that the Kob-Andersen Lennard-Jones system has well-satisfied off-equilibrium scaling properties in heating (expansion) protocols as found for cooling (compression) procedures [12,15].

In Fig. 2 we show how the FDR changes as the initial T in the up jump is changed. The time scales investigated here are the same as those in Fig. 1. Upon increasing the initial T the deviation from the FDT is weaker making it clear why low- T initial states are necessary for our study. However it is interesting to note that, even for an initial $T > T_{\text{MCT}}$, the deviation from the FDT is still quite evident. This suggests that the FDT violation can be observed in a wide range of temperatures in the supercooled regime above and below T_{MCT} .

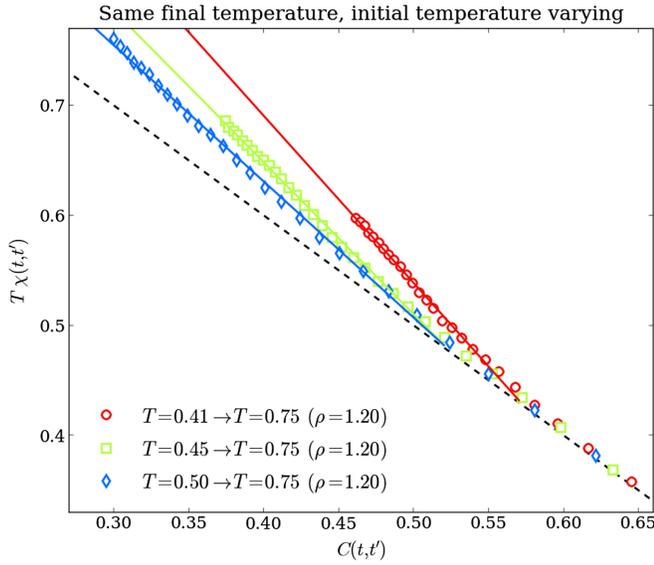


FIG. 2 (color online). FD plots for T up jumps starting with different initial temperatures ($6 \times 10^2 < t' < 8 \times 10^3$ MC steps). Notice that as the initial temperature is increased the deviation from the FDT reduces.

To further characterize the time dependence of the FDT violation we choose as initial equilibrium state $T = 0.41$ and as a final state $T = 0.75$ ($\rho = 1.2$). In this jump the time evolution of the system is slow enough to allow for a characterization of the FDR at well-separated aging times. Note that t varies from 5×10^3 to 1.2×10^4 MC steps while, for each fixed t , we let t' vary from $\sim t/10$ to t . As shown in Fig. 3 we find that X strongly depends on time suggesting that, as the system equilibrates, the deviation from the FDT decreases and the T_{eff} smoothly approaches the bath temperature T_{bath} . This dynamic behavior of the FDR gives the possibility of studying in detail the connection between T_{eff} and the configuration space visited out of equilibrium. In the inherent state (IS) formalism [32,33] each configuration of the system is associated with the configuration reached by a steepest descent minimization of the potential energy. The phase space is partitioned in basins of attraction of different potential energy minima. In the IS formalism, the free energy is written as $F = e_{\text{IS}} - T_{\text{bath}} s_{\text{conf}}(e_{\text{IS}}) + f_{\text{vib}}(e_{\text{IS}}, T_{\text{bath}})$, where the configurational entropy s_{conf} measures the number of distinct minima with energy e_{IS} while the vibrational free-energy f_{vib} accounts for the contribution to the total free energy arising from the exploration of the sampled basin volume in configuration space. Such a free-energy expression is the IS analog of the Thouless-Anderson-Palmer free energy [34], where e_{IS} labels the possible Thouless-Anderson-Palmer states. A convenient way to calculate $\partial s_{\text{conf}}/\partial e_{\text{IS}}$, a quantity that will be used later on, is offered by the equilibrium property $\partial F/\partial e_{\text{IS}} = 0$:

$$\frac{\partial s_{\text{conf}}}{\partial e_{\text{IS}}} = T_{\text{bath}}^{-1} \left[1 + \frac{\partial f_{\text{vib}}(e_{\text{IS}}, T_{\text{bath}})}{\partial e_{\text{IS}}} \right]. \quad (2)$$

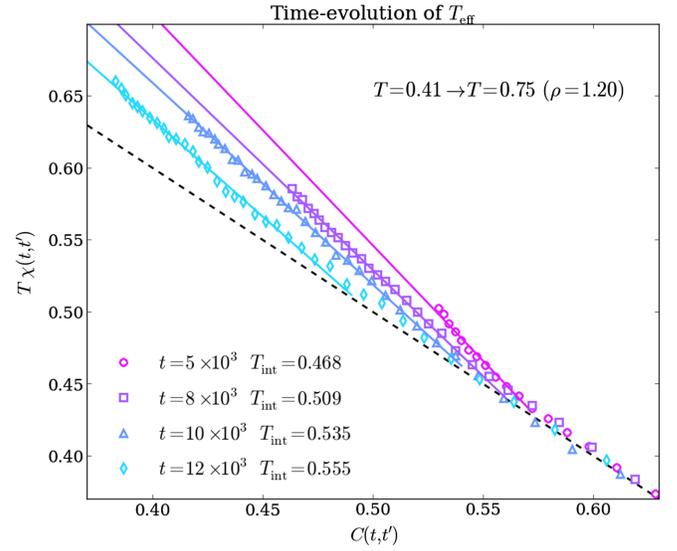


FIG. 3 (color online). FD plots for several T up jumps as the time t increases. Here t' varies always from $\sim t/10$ to t . The deviation from the FDT (dashed line) gradually decreases as t increases suggesting that the slow degrees of freedom of system slowly thermalize to the bath temperature. The straight lines have slope $-T_{\text{bath}}/T_{\text{int}}(t)$ (only the intercept has been adjusted for fitting), where T_{int} is the internal temperature obtained by using Eq. (4) [14] (see text).

In the IS framework the aging dynamics is modeled as a walk in configuration space, composed by a fast vibration in one minimum and rare jumps among different minima. Under the assumption that during aging the system explores the same basins visited in equilibrium (but see Ref. [35]), it is possible to define an off-equilibrium extension of the free-energy F in which the configurational part is weighted by the internal T of the system T_{int} (the analog of the effective temperature) while the vibrational term is assumed to be in equilibrium with the bath temperature [14]. This results in $F = e_{\text{IS}} - T_{\text{int}} s_{\text{conf}}(e_{\text{IS}}) + f_{\text{vib}}(e_{\text{IS}}, T_{\text{bath}})$. By analogy with standard thermodynamics T_{int} can be obtained by minimizing the free energy with respect to e_{IS} :

$$\frac{\partial F}{\partial e_{\text{IS}}} = 1 - T_{\text{int}} \frac{\partial s_{\text{conf}}(e_{\text{IS}})}{\partial e_{\text{IS}}} + \frac{\partial f_{\text{vib}}(e_{\text{IS}}, T_{\text{bath}})}{\partial e_{\text{IS}}} = 0. \quad (3)$$

To calculate T_{int} we evaluate e_{IS} in equilibrium as a function of T (Fig. 4, left panel). Then we invert the function $e_{\text{IS}}(T)$ to determine the temperature at which basins, of the same depth as the one explored in aging, are typically populated in equilibrium. We indicate such T with T_{eq} . Noting that in equilibrium T_{bath} coincides with T_{eq} , it is possible to combine Eqs. (2) and (3) to find [14]

$$T_{\text{int}}(e_{\text{IS}}) = T_{\text{eq}}(e_{\text{IS}}) \frac{1 + \frac{\partial f_{\text{vib}}(e_{\text{IS}}, T_{\text{bath}})}{\partial e_{\text{IS}}}}{1 + \frac{\partial f_{\text{vib}}(e_{\text{IS}}, T_{\text{eq}}(e_{\text{IS}}))}{\partial e_{\text{IS}}}}. \quad (4)$$

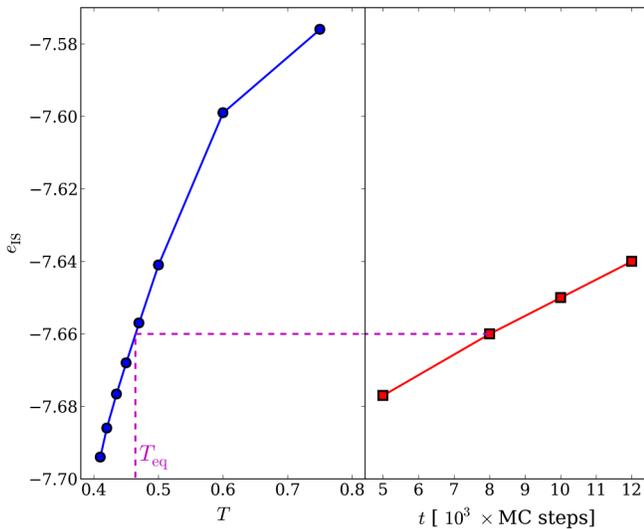


FIG. 4 (color online). Left: Average inherent structure energy in equilibrium as a function of T . Right: Average inherent structure energy after a T up jump ($T = 0.41 \rightarrow T = 0.75$, $\rho = 1.20$) as a function of time. By performing the construction indicated by the dashed line, it is possible to relate the aging time t with T_{eq} , i.e., the T at which basins of the same depth as the one visited during aging are explored in equilibrium. After correcting for the vibrational contribution [Eq. (4)], we obtain a value for the internal temperature T_{int} that compares very well the FDT violation (see Fig. 3).

Note that if the landscape were composed by basins with the same shape (which would imply $\partial f_{vib}/\partial e_{IS} = 0$), then $T_{int}(e_{IS}) = T_{eq}(e_{IS})$. Following Ref. [14] we determine f_{vib} in equilibrium simulations by approximating the IS minima as harmonic 3N-dimensional wells. The T_{int} value computed via Eq. (4) for different aging times can be compared with the slope of the FDR. Results displayed in Fig. 3 show that, to a very good approximation, $T_{eff}(t) = T_{int}(t)$, supporting the thermodynamic link implied in the FDR approach. These results suggest that, even in a T up jump, T_{eff} is connected to the dynamics of the underlying IS [14,15]. We also note that the harmonic approximation for f_{vib} , that is expected to be less accurate as T is increased, still leads to very reasonable results.

Conclusions.—We have investigated the off-equilibrium dynamics of a deeply supercooled atomic liquid following an instantaneous increase of the bath temperature. Relying on GPU-implemented numerical simulations we have focused on the FDR and the effective temperature that can be measured out of equilibrium. We have shown that FDR is characterized by the typical two-step shape associated with the time scale separation of glassy dynamics. The violation factor is found to be greater than one giving a T_{eff} lower than T_{bath} temperature that is the opposite of what is found upon cooling a liquid in the glassy phase. We have identified the most suitable equilibrium states among which the temperature up jump has to be performed to

observe and characterize in detail the FDR. The effective temperature measured displays a clear time dependence. Further analysis indicates that T_{eff} coincides to a good approximation with the internal temperature obtained by an extended (off-equilibrium) thermodynamic framework based on the potential energy phase-space decomposition.

Our results suggest a new route to follow in the experimental study of the FDR. In these challenging experiments one has indeed to measure independently response and correlation as the temperature is quickly changed. The temperature change has to be very fast with respect to the relaxation time of the system. One possibility suggested by our results is to try to perform a heating experiment among equilibrium liquid states that can be quite easily prepared experimentally. These experiments will possibly take advantage of the fact that rapidly heating the liquid might be much easier than cooling if the heating is performed by using, for example, some laser-based techniques [36,37]. It could be, quite unexpectedly, that the concepts of fluctuation dissipation relation and effective temperature, that were conceived for characterizing the fast cooling of a liquid, are instead more easily accessible in a heating experiment.

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