Extension of the Fluctuation-Dissipation Theorem to the Physical Aging of a Model Glass-Forming Liquid

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We present evidence in favor of the possibility of treating an out-of-equilibrium supercooled simple liquid as a system in quasiequilibrium. Two different temperatures, one controlled by the external bath and one internally selected by the system, characterize the quasiequilibrium state. The value of the internal temperature is explicitly calculated within the inherent structure thermodynamic formalism. We find that the internal temperature enters the relation between the response to an external perturbation and the long-time decay of fluctuations in the liquid.

The slow dynamics of supercooled liquids on approaching the glass transition is one of the most interesting topics in condensed matter. Their characteristic structural relaxation time varies by more than 13 orders of magnitude in a small temperature range, thus becoming comparable to the observation time at the glass transition temperature T_g [1–3]. Following a T jump from above to below T_g, the system equilibration times exceed laboratory time scales and its properties depend on the time spent in the glass state. This phenomenon, known as physical aging, highlights the extremely slow equilibration processes observed in glasses.

In recent years, the thermodynamic approach to the glass transition has been at the center of novel theoretical [4–8] and numerical studies [9–14], aiming to clarify the connections between dynamics and thermodynamics and the origin of the slowing down of the equilibration processes. A detailed thermodynamic description of supercooled liquids [15] has been developed, based on information on the topology of the potential energy surface, such as the number and depth of the local minima of the potential energy surface, the so-called inherent structures (IS). In this framework, the short-time dynamics of the supercooled liquids has been associated with the intrabasin motion (*ps*-time scale), while the long-time slow dynamics to the interbasin motion. This time-scale separation between fast intrabasin and slow interbasin dynamics appears clearly in the proposed expression for the constant volume liquid free energy $F(T)$ [15]:

$$F(T) = -TS_{\text{conf}}[e_{\text{IS}}(T)] + f_{\text{basin}}[T, e_{\text{IS}}(T)], \quad (1)$$

where $-TS_{\text{conf}}(e_{\text{IS}})$ accounts for the entropic contribution arising from the number of basins of potential energy depth e_{IS} and $f_{\text{basin}}(T, e_{\text{IS}})$ describes the free energy of the system constrained in one characteristic e_{IS} basin [16]. The above expression for F shows that following a T jump the equilibration process involves both the (fast) equilibration of the intrabasin degrees of freedom with the bath temperature T_{bath} as well as the (slow) motion of the system searching for basins of appropriate depth in configuration space.

During this process, the system slowly transfers energy to the bath, as it explores basins of lower and lower e_{IS}. The equilibration process is completed when e_{IS} reaches its equilibrium value $e_{\text{IS}}(T_{\text{bath}})$.

The value of e_{IS} in equilibrium can be calculated imposing the condition of F being a minimum, i.e., solving

$$\frac{\partial F}{\partial e_{\text{IS}}} = -T \frac{\partial S_{\text{conf}}(e_{\text{IS}})}{\partial e_{\text{IS}}} + \frac{\partial f_{\text{basin}}(T, e_{\text{IS}})}{\partial e_{\text{IS}}} = 0, \quad (2)$$

where $\partial f_{\text{basin}}/\partial e_{\text{IS}}$ describes the free energy change associated with the change in the basin shape with e_{IS} and $\partial S_{\text{conf}}/\partial e_{\text{IS}}$ the entropic change associated with the different basin degeneracy.

In this Letter, we present an extension of the thermodynamics formalism to the case of an out-of-equilibrium supercooled liquid [7]. We show that such an extension allows us to predict the response of the (aging) system to an external perturbation and the way this response depends on the time spent in the low-temperature glass state. The analysis is based on the assumption that the separation of intrabasin and interbasin time scales—which characterize equilibrium supercooled liquid states—retains its validity during aging. The results support the possibility that an aging liquid, notwithstanding its out-of-equilibrium condition, can still be described as a system in quasiequilibrium. The price one pays is the introduction of an internal temperature [17] which is a function both of the thermostat temperature and of the (*t*-dependent) state of the system, expressed by its e_{IS} value. The introduced T defines more precisely the concept of fictive temperature, usually defined by the experimentalists as the T at which the ergodicity of the system was broken [18]. Our results also support the idea that the slow search for the low energy minima in configuration space is the essential feature of aging phenomena in liquids.

The model liquid we study is the Lennard-Jones binary (80:20) mixture (BMLJ) which has been extensively investigated in the past [19,20]. For this model, the basin degeneracy and the basin free energy have been calculated [13]. Figure 1 shows the T dependence of $f_{\text{basin}}(T, e_{\text{IS}})$
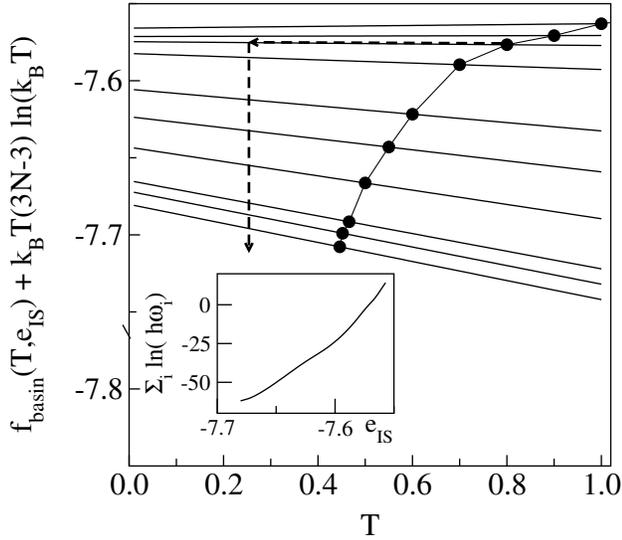
FIG. 1.   Basin free energy for the BMLJ system in harmonic approximation. Each of the dashed lines shows $f_{\text{basin}}(e_{\text{IS}}, T)$ for one specific e_{IS} value (the corresponding e_{IS} value coincides with the $T = 0$ value of f_{basin}). In all curves, the e_{IS}-independent contribution $(3N - 3)k_B T \ln(k_B T)$ [see Eq. (3)] has not been included for clarity reasons. Filled circles are the equilibrium values $f_{\text{basin}}[e_{\text{IS}}(T), T]$. The arrows indicate the path followed by the system after a quench from $T = 0.8$ to $T_{\text{bath}} = 0.25$. The inset shows the e_{IS} dependence of $\sum_{i=1}^{3N-3} \ln(\hbar\omega_i)$. The value of $\hbar$ is such that the dimension of $\hbar\omega$ (as well as the dimension of $k_B T$) is in units of the LJ potential depth [20].

for a few selected e_{IS} values. The intrabasin free energy f_{basin} has been evaluated in harmonic approximation, expanding the potential energy around the local minimum, as

$$f_{\text{basin}}(T, e_{\text{IS}}) = e_{\text{IS}} + k_B T \sum_{i=1}^{3N-3} \ln[\hbar\omega_i(e_{\text{IS}})/k_B T], \quad (3)$$

where ω_i is the ith normal mode frequency. Recently, the out-of-equilibrium dynamics in model liquids, following a T jump, has been studied [21–24]. Reference [24] suggested the possibility that the equilibration in configuration space proceeds via quasiequilibrium steps. Such an equilibration process is schematically depicted with arrows in Fig. 1, for the case of a jump from $T = 0.8$ to $T_{\text{bath}} = 0.25$. In a time much shorter than any basin change, f_{basin} assumes the value characteristic of the final bath temperature (full line arrow in Fig. 1), but on the same e_{IS} basin. The fast equilibration of the intrabasin degrees of freedom is followed by a much slower process (dashed arrow in Fig. 1) during which the system populates deeper and deeper basins. The slow time dependence of e_{IS} is reported in Fig. 2(right).

Within the hypothesis of quasiequilibrium, the system free energy after a time t from the quench—when the system is populating basins of depth $e_{\text{IS}}(t)$—can be expressed again as in Eq. (1) [7]. The vibrational part is unambiguously given by $f_{\text{basin}}[e_{\text{IS}}(t), T_{\text{bath}}]$, since the intrabasin degrees of freedom quickly equilibrate with the
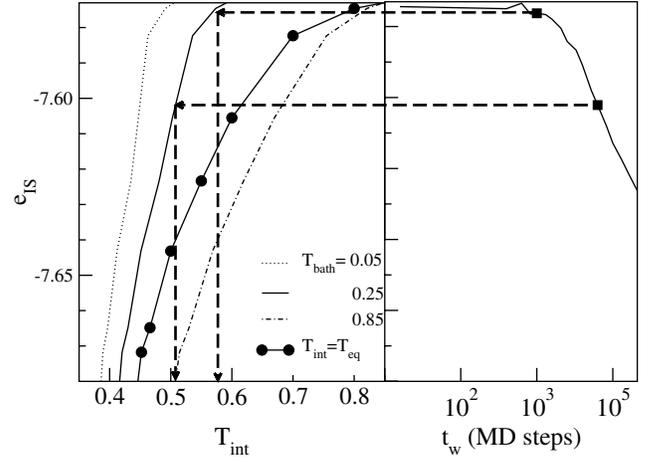
FIG. 2.   Left: solutions of Eq. (4) for several T_{bath} values for the studied BMLJ system. Right: e_{IS} as a function of time, following a T jump from $T = 0.8$ to $T_{\text{bath}} = 0.25$ [28]. The arrows show graphically the procedure which connects the $e_{\text{IS}}(t)$ value to the T_{int} value, once T_{bath} is known. Note that if the curvature of the basins was independent on e_{IS}, then curves for different T_{bath} would all coincide with $T_{\text{eq}}(e_{\text{IS}})$, i.e., with the T at which in equilibrium the basin of depth e_{IS} is populated (filled symbols).

thermostat at T_{bath}. The entropic contribution to the free energy requires the definition of an internal temperature T_{int}, higher than the thermostat temperature [17], to reflect the out-of-equilibrium condition and the flow of heat from the system to the thermostat. To evaluate the internal temperature $T_{\text{int}}(e_{\text{IS}}, T_{\text{bath}})$ selected by the system when it is populating basins of depth e_{IS} we search for solutions of Eq. (2) but, in contrast to the equilibrium case, we consider the value e_{IS} to be fixed and solve for the unknown temperature, obtaining

$$T_{\text{int}}(e_{\text{IS}}, T_{\text{bath}}) = \frac{\frac{\partial}{\partial e_{\text{IS}}} f_{\text{basin}}(T_{\text{bath}}, e_{\text{IS}})}{\frac{\partial}{\partial e_{\text{IS}}} S_{\text{conf}}(e_{\text{IS}})}. \quad (4)$$

Note that, differently from Eq. (2), f_{basin} is now evaluated at the thermostat temperature T_{bath}. This expression for T_{int} coincides with the expression proposed by Franz and Virasoro [25] in the context of p-spin systems, once the basin free energy is identified with the Thouless-Anderson-Palmer free energy [26]. We note that $\partial S_{\text{conf}}/\partial e_{\text{IS}}$ can be evaluated from the known T dependence of e_{IS} in equilibrium by solving Eq. (2), and, thus, once a model for f_{basin} is chosen, $T_{\text{int}}(e_{\text{IS}}, T_{\text{bath}})$ can be explicitly calculated. If T_{bath} is small (as it usually is in the glass state), the harmonic approximation for f_{basin} can be confidently used. In this case, calling $T_{\text{eq}}(e_{\text{IS}})$ the temperature at which basins of depth e_{IS} are populated in equilibrium, from Eq. (4) and Eq. (2) T_{int} can be calculated as

$$T_{\text{int}}(e_{\text{IS}}, T_{\text{bath}}) = \frac{1 + k_B T_{\text{bath}} \sum_i \frac{\partial \ln[\hbar\omega_i/k_B T_{\text{bath}}]}{\partial e_{\text{IS}}}}{1 + k_B T_{\text{eq}}(e_{\text{IS}}) \sum_i \frac{\partial \ln[\hbar\omega_i/k_B T_{\text{eq}}]}{\partial e_{\text{IS}}}} \times T_{\text{eq}}(e_{\text{IS}}). \quad (5)$$

Figure 2(left) shows $T_{int}(e_{IS}, T_{bath})$ for the BMLJ system. We note that, if basin curvatures were independent on the e_{IS} value, then the derivatives in Eq. (5) would be zero. Hence, $T_{int}(e_{IS}, T_{bath})$ would not depend on T_{bath} and T_{int} would coincide with $T_{eq}(e_{IS})$. In this limit, T_{int} plays the same role as the fictive temperature introduced in the analysis of experimental data in aging systems [18].

The expression for $T_{int}(e_{IS}, T_{bath})$ [Fig. 2(left)] together with $e_{IS}(t)$ [Fig. 2(right)], if considered parametrically in e_{IS}, models the time dependence of T_{int}. If, within the observation time the system is capable to reach equilibrium (for example, when $T_{bath} > T_g$), then the value of T_{int} for long times coincides with T_{bath}. In a T jump from above to below T_g, assuming that the system is capable to equilibrate in configuration space only down to $e_{IS}(T_g)$, the long time limit of T_{int} will be given by $T_{int}[T_{bath}, e_{IS}(T_g)]$ a value different from T_g. Hence T_{int} is related to but does not coincide with T_g, the temperature at which equilibrium was lost.

To test the predictions of Eqs. (4) and (5), i.e., the assumption of quasiequilibrium in the aging system, an independent calculation of T_{int} is required. A possible way to force the system to reveal its internal temperature is offered by the well-known relation between response to an external perturbation and decay of correlation in thermal equilibrium. With this aim we study the response of the liquid, described by the Hamiltonian H_0, to an external perturbation switched on at $t = t_w$. If the perturbation adds the term $H_P = -V_o B(\mathbf{r^N}) \theta(t - t_w)$ to the Hamiltonian [where $\theta(t)$ is the Heaviside step function], linear response theory predicts that the time evolution of any variable $A(\mathbf{r^N})$ conjugated to B is [27]

$$\langle A(\tau) \rangle_P = -\frac{V_o}{k_B T} [\langle A(\tau) B(0) \rangle_0 - \langle A(0) B(0) \rangle_0], \quad (6)$$

where $\tau \equiv t - t_w$, $\langle \cdots \rangle_P$ is the ensemble average over the perturbed system ($H_0 + H_P$), and $\langle \cdots \rangle_0$ is the ensemble average over the unperturbed one (H_0). Equation (6) shows that the amplitude of the perturbation is proportional to T^{-1} and thus offers an *independent* way to calculate the internal temperature of the system. We chose $B \equiv (\rho_\mathbf{k}^\alpha + \rho_\mathbf{k}^{\alpha*})$, where $\rho_\mathbf{k}^\alpha \equiv \sum_i^{N_\alpha} e^{i\mathbf{k} \cdot \mathbf{r}_i^\alpha}/\sqrt{N}$ is the Fourier transform of the density of α particles at wave vector $\mathbf{k}$, and study the response of $A \equiv \rho_\mathbf{k}^\alpha$. In this case, $\langle A(t)B(0) \rangle_0$ coincides with the dynamical structure factor $S_\mathbf{k}^{\alpha\alpha}(t) \equiv \langle \rho_\mathbf{k}^\alpha(t) \rho_\mathbf{k}^{\alpha*}(0) \rangle_0$. Thus, with the present choice of A and B, linear response theory predicts [27]

$$\langle \rho_\mathbf{k}^\alpha(\tau) \rangle = -\frac{V_o}{k_B T} [S_\mathbf{k}^{\alpha\alpha}(\tau) - S_\mathbf{k}^{\alpha\alpha}(0)]. \quad (7)$$

Equation (7)—one of the forms of the fluctuation-dissipation theorem—offers the possibility to test the quasiequilibrium hypothesis. Indeed, for short τ (i.e., in the time region where the correlation function assumes values between the initial and the plateau values) $S_\mathbf{k}^{\alpha\alpha}(\tau)$

probes the intrabasin dynamics and hence the relation between correlation and response, Eq. (7), will be controlled by $-V_o/k_B T_{bath}$. Similarly, for long times (i.e., in the time region where the correlation function assumes values smaller than the plateau value) $S_\mathbf{k}^{\alpha\alpha}(\tau)$ probes the interbasin dynamics and the relation will be controlled by $-V_o/k_B T_{int}$. Hence, the value of the slope of $\langle \rho_\mathbf{k}^\alpha(\tau) \rangle$ vs $S_\mathbf{k}^{\alpha\alpha}(\tau)$ will change from $-V_o/k_B T_{bath}$ to $-V_o/k_B T_{int}$. The value of T_{bath} is fixed by the thermostat while the value of T_{int} will depend on which e_{IS} basin the system is populating when the external field is switched on.

Thus, when switching on the perturbing field while the system is populating basins of depth e_{IS}, we predict that $T_{int}(e_{IS}, T_{bath})$, Eq. (4), will coincide with the temperature calculated from the slope of $\langle \rho_\mathbf{k}^\alpha(\tau) \rangle$ vs $S_\mathbf{k}^{\alpha\alpha}(\tau)$, for times longer than the intrabasin dynamics.

Figure 3(left) shows $S_\mathbf{k}^{\alpha\alpha}(\tau)$ and $\langle \rho_\mathbf{k}^\alpha(\tau) \rangle$ switching the perturbing field on at two different t_w, and hence for two different initial e_{IS} values. The reported data refer to a relaxation process, from an initial temperature of $T = 0.8$ to $T_{bath} = 0.25$. Data are averaged over 300 different quench realizations and over more than 60 different independent perturbations H_P (with the same k modulus) for each quench realization [28]. Both $S_\mathbf{k}^{\alpha\alpha}(\tau)$ and $\langle \rho_\mathbf{k}^\alpha(\tau) \rangle$ show the two-step relaxation characteristic of the supercooled state, which has been associated with the separation of intrabasin and interbasin motion. Figure 3(right) shows the corresponding response vs correlation plots, Eq. (7). At short times (intrabasin motion), $\langle \rho_\mathbf{k}(t) \rangle$ vs $S_\mathbf{k}(t)$ is linear with the expected T_{bath}^{-1} slope, properly describing the equilibrium condition of the vibrational dynamics with the external reservoir. At larger times, the interbasin motion sets in and, as shown by the full lines in Fig. 3(right),
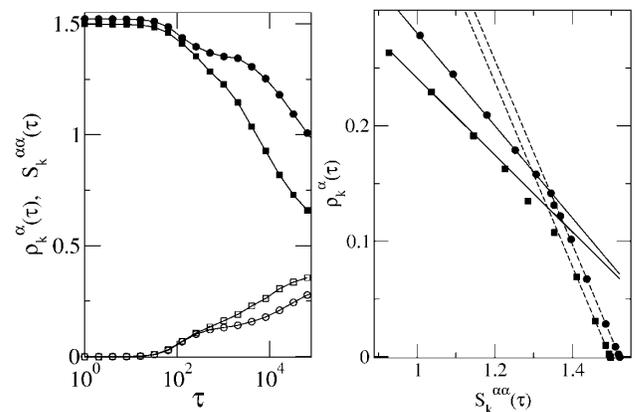
FIG. 3. Left: time dependence of the response (ρ_k^α, open symbols) and correlation function ($S_k^{\alpha\alpha}$, filled symbols) for $t_w = 1024$ (circles) and $t_w = 16\,384$ (squares). Right: parametric plot (in τ) of ρ_k^α vs $S_k^{\alpha\alpha}$ for the two studied t_w. Dashed lines have slope $V_o/k_B T_{bath}$ (with $T_{bath} = 0.25$), solid lines have slope $V_o/k_B T_{int}[e_{IS}(t_w = 1024) = -7.576, T_{bath} = 0.25]$, and $V_o/k_B T_{int}[e_{IS}(t_w = 16\,384) = -7.602, T_{bath} = 0.25]$, according to Eq. (4). The two T_{int} values can be read off from Fig. 2. The modulus of k is 6.7 [28].

the slope of $\langle \rho_{\mathbf{k}}^{\alpha}(\tau) \rangle$ vs $S_{\mathbf{k}}^{\alpha\alpha}(\tau)$ is extremely well predicted by the values of T_{int} calculated according Eq. (5).

The good agreement between the T measured by the amplitude of the response of the aging system to the external perturbation and the T predicted theoretically using the IS thermodynamics formalism supports the main hypothesis on which our analysis is based, i.e., the validity of the quasiequilibrium condition.

Concluding, we recall that the time window accessed by the numerical experiments is very different from the experimental one and hence measurements of the internal temperature in aging experiments [29] are very valuable to assess the range of validity of the presented approach. We also stress that the detailed analysis presented in this Letter for a structural glass is conceptually identical to the analysis performed in recent years to describe the out-of-equilibrium dynamics of disordered spin models [30]. However, we prefer to present our results in terms of extended validity (as opposed to violation) of the fluctuation dissipation theorem. Recent tests on finite-size disordered p-spin systems also support the validity of the thermodynamic approach to aging [31].

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