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Test of nonequilibrium thermodynamics in glassy systems: The soft-sphere case

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The scaling properties of the soft-sphere potential allow the derivation of an exact expression for the pressure of a frozen liquid, i.e., the pressure corresponding to configurations which are local minima in its multidimensional potential energy landscape. The existence of such a relation offers the unique possibility for testing the recently proposed extension of the liquid free energy to glassy out-of-equilibrium conditions and the associated expression for the temperature of the configurational degrees of freedom. We demonstrate that the nonequilibrium free energy provides an exact description of the soft-sphere pressure in glass states.

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The potential energy landscape (PEL) formalism [1] has provided a transparent formulation of the equilibrium free energy of supercooled liquids based on the statistical properties of a system's multidimensional potential energy surface [1–8], i.e., in terms of the number, depth, and associated phase-space volume of local potential energy minima [9]. This formalism, in which the PEL minima are termed inherent structures (IS), is well suited for the description of supercooled liquids and glasses. While the liquid explores an exponentially large number of distinct PEL basins, a glass explores only a very small fraction of these (within an experimentally accessible time frame.) The equilibrium free energy for the whole system is written as sum of two contributions: an entropic term $-TS_{\mathrm{conf}}(E_{\mathrm{IS}})$, which accounts for the number of basins of depth E_{IS}, and the term $E_{\mathrm{IS}}+F_{\mathrm{vib}}(T,E_{\mathrm{IS}})$, which describes the free energy of the system confined to an average basin of depth E_{IS}. Here, S_{conf} is associated with the energy degeneracy of mechanically stable configurations and hence is termed the configurational entropy, while F_{vib} is associated with the "vibrational," kinetic distortions of the system around these configurations. Analogous expressions have been derived from alternative theoretical approaches [10–13].

In this paper, we first show that a PEL-based expression for the out-of-equilibrium thermodynamics of glassy systems provides an expression for the thermodynamic pressure of inherent structures, that is, the pressure corresponding to the ensemble of potential energy minima whose basins are sampled at a given temperature and density. We then show that for a particular potential energy function corresponding to a system of soft spheres, one can verify that the mechanical pressure calculated from the change of energy experienced by an inherent structure configuration upon compression is exactly equivalent to the proposed thermodynamic expression derived from out of equilibrium arguments. This equivalence of mechanical and thermodynamic treatments for soft spheres provides support for the out-of-equilibrium framework and suggests that the expression for IS pressure is general to arbitrary systems.

The extension of the supercooled liquid free energy to the out-of-equilibrium case has recently been proposed [12,14–18]. In the PEL formalism, out-of-equilibrium conditions are implemented by imposing the constraint that the basin explored by the system while aging does not coincide with the typical equilibrium one [17]. The proposed free energy is given by

$$F(V,T,T_{\mathrm{e}})=-T_{\mathrm{e}}S_{\mathrm{conf}}(V,E_{\mathrm{IS}})+E_{\mathrm{IS}}+F_{\mathrm{vib}}(V,T,E_{\mathrm{IS}}). \tag{1}$$

The main distinction between this expression and the equilibrium case is that while F_{vib} is still evaluated at the thermostat temperature T, the configurational entropy term is weighted by an additional temperature T_{e}, which may be thought of as the temperature of the (out-of-equilibrium) configurational degrees of freedom. This is a consequence of the fact that when the system is aging, only the fast degrees of freedom (related to the vibrational contributions to F) quickly equilibrate to the bath temperature. The slow configurational degrees of freedom are assumed to equilibrate via a sequence of quasiequilibrium steps. As a consequence, the configurational entropy is weighed by a temperature different from the bath T.

Note that the existence of two different temperatures controlling the thermodynamics of an aging system modifies the classical thermodynamics relations, and the new relations reduce to the classical ones only when the system reaches equilibrium and T_{e} and T coincide. When T_{e} and T differ, the system is in a nonequilibrium state. While in equilibrium the value of E_{IS} is controlled only by T and V via the condition $\partial F(T,V)/\partial E_{\mathrm{IS}}=0$, in this nonequilibrium setting the value of E_{IS} is also a function of T_{e}. In this case the basin depth sampled by the system, $E_{\mathrm{IS}}(V,T,T_{\mathrm{e}})$, is the solution of

$$1+\frac{\partial F_{\mathrm{vib}}}{\partial E_{\mathrm{IS}}}-T_{\mathrm{e}}\frac{\partial S_{\mathrm{conf}}}{\partial E_{\mathrm{IS}}}=0. \tag{2}$$

This expression is based on the hypothesis that the out-of-equilibrium system samples a distribution of basins simi-

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lar to the one explored in equilibrium [14–17]. Inverting $E_{\mathrm{IS}}(V,T,T_{\mathrm{e}})$ provides an estimate of T_{e} when the bath temperature is T and the system is confined to a basin of depth E_{IS}. As already discussed [17], the expression for T_{e} coincides with the experimentally determined fictive temperature [19] for models in which $\partial F_{\mathrm{vib}}/\partial E_{\mathrm{IS}}=0$, i.e., when the phase-space volume of basins is independent of their depth. The same expression for T_{e} has been derived also by Franz and Virasoro [16] in the context of p-spin systems, once the basin free energy is identified with the Thouless-Anderson-Palmer free energy [10].

Starting from the proposed free energy [Eq. (1)] it is possible to calculate the thermodynamic pressure in out-of-equilibrium conditions, when the bath temperature is T and the configurational temperature is T_{e} (i.e., when the system is exploring basins different from those explored in equilibrium at temperature T). To this end, we evaluate the constant-T volume derivative of the free energy in Eq. (1),

$$P(V,T,T_{\mathrm{e}})=-\left(\frac{\partial F(V,T,T_{\mathrm{e}})}{\partial V}\right)_{T,T_{\mathrm{e}}} \tag{3}$$

$$\begin{aligned}&=T_{\mathrm{e}}\left[\left(\frac{\partial S_{\mathrm{conf}}}{\partial E_{\mathrm{IS}}}\right)_V\left(\frac{\partial E_{\mathrm{IS}}}{\partial V}\right)_{T,T_{\mathrm{e}}}+\left(\frac{\partial S_{\mathrm{conf}}}{\partial V}\right)_{E_{\mathrm{IS}}}\right]\\&\quad-\left(\frac{\partial E_{\mathrm{IS}}}{\partial V}\right)_{T,T_{\mathrm{e}}}-\left(\frac{\partial F_{\mathrm{vib}}}{\partial E_{\mathrm{IS}}}\right)_{T,V}\left(\frac{\partial E_{\mathrm{IS}}}{\partial V}\right)_{T,T_{\mathrm{e}}}\\&\quad-\left(\frac{\partial F_{\mathrm{vib}}}{\partial V}\right)_{T,E_{\mathrm{IS}}},\end{aligned} \tag{4}$$

and rearranging

$$\begin{aligned}P(V,T,T_{\mathrm{e}})&=\left(\frac{\partial E_{\mathrm{IS}}}{\partial V}\right)_{T,T_{\mathrm{e}}}\left[T_{\mathrm{e}}\left(\frac{\partial S_{\mathrm{conf}}}{\partial E_{\mathrm{IS}}}\right)_V-1-\left(\frac{\partial F_{\mathrm{vib}}}{\partial E_{\mathrm{IS}}}\right)_{T,V}\right]\\&\quad+T_{\mathrm{e}}\left(\frac{\partial S_{\mathrm{conf}}}{\partial V}\right)_{E_{\mathrm{IS}}}-\left(\frac{\partial F_{\mathrm{vib}}}{\partial V}\right)_{T,E_{\mathrm{IS}}}.\end{aligned} \tag{5}$$

The first term on the right-hand side of Eq. (5) is zero by the E_{IS} condition in Eq. (2). Thus,

$$P(V,T,T_{\mathrm{e}})=T_{\mathrm{e}}\left(\frac{\partial S_{\mathrm{conf}}}{\partial V}\right)_{E_{\mathrm{IS}}}-\left(\frac{\partial F_{\mathrm{vib}}}{\partial V}\right)_{T,E_{\mathrm{IS}}}. \tag{6}$$

The above expression, when evaluated at the bath temperature $T=0$ K, provides the theoretical expression for the pressure experienced in an inherent structure, P_{IS}. Indeed, an infinite cooling rate quench to $T=0$ K brings the system to the local inherent structure [1,20]. In other words, the steepest descent procedure used numerically to locate an inherent structure is equivalent to the physical process of setting the bath temperature to $T=0$ K. The absolute zero bath temperature eliminates any contribution arising from the vibrational free energy and hence, $P_{\mathrm{IS}}(V,E_{\mathrm{IS}})$ is

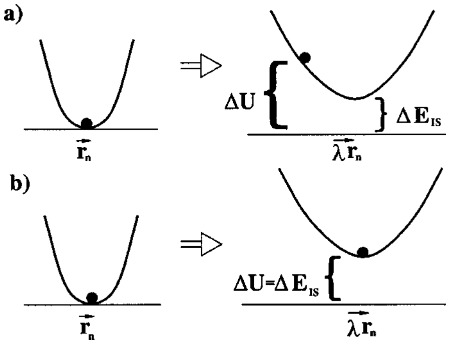

FIG. 1. Results of a uniform scaling of particle coordinates for an inherent structure configuration: (a) the case for a generic potential, for which the change in potential energy ΔU is not equal to the change in inherent structure energy ΔE_{IS}; (b) the soft-sphere potential, for which $\Delta U=\Delta E_{\mathrm{IS}}$.

$$P_{\mathrm{IS}}(V,E_{\mathrm{IS}})=P(V,0,T_{\mathrm{e}})=T_{\mathrm{e}}\left(\frac{\partial S_{\mathrm{conf}}}{\partial V}\right)_{E_{\mathrm{IS}}}. \tag{7}$$

Using the mathematical identity

$$\left(\frac{\partial S_{\mathrm{conf}}}{\partial V}\right)_{E_{\mathrm{IS}}}=-\left(\frac{\partial S_{\mathrm{conf}}}{\partial E_{\mathrm{IS}}}\right)_V\left(\frac{\partial E_{\mathrm{IS}}}{\partial V}\right)_{S_{\mathrm{conf}}}, \tag{8}$$

and the E_{IS} condition in Eq. (2) evaluated at $T=0$, we obtain

$$P_{\mathrm{IS}}(V,E_{\mathrm{IS}})=-T_{\mathrm{e}}\left(\frac{\partial S_{\mathrm{conf}}}{\partial E_{\mathrm{IS}}}\right)_V\left(\frac{\partial E_{\mathrm{IS}}}{\partial V}\right)_{S_{\mathrm{conf}}}=-\left(\frac{\partial E_{\mathrm{IS}}}{\partial V}\right)_{S_{\mathrm{conf}}}, \tag{9}$$

which provides an alternative definition of the inherent structure pressure.

Note that the mechanical definition of P_{IS}, that is the measure of the energy change of the system under the compression of an IS configuration, does not necessarily coincide with Eq. (9) which is a derivative of the IS energy at constant configurational entropy. Indeed, in general, on isotropically compressing an IS configuration, the compressed state is not a local minima of the potential energy surface and hence, the change in IS energy is only a fraction of the energy change on compression [see Fig. 1(a)]. We also note that the configurational entropy of the system is not constant during the compression, since the number of basins and their distribution in energy is function of V. In other words, while the mechanical definition of pressure relates to the potential difference due to a differential scaling of configurational coordinates, in general, the response of E_{IS} due to an infinitesimal volume change does not correspond to such a continuous configurational deformation, but instead to a differential change in the ensemble of minima considered.

We now show that, for the soft-sphere potential, the change in energy associated with compression of an IS configuration does coincide with the change of IS energy and that the configurational entropy does not change on compression, providing a consistency check for the derived expression for $P_{\rm IS}$ and, more importantly, providing support for Eqs. (1) and (2). The soft-sphere potential has been extensively studied as a model for liquids and glasses [8,21–29]. The potential energy E of a system composed of N particles interacting via a soft-sphere potential is $E(\mathbf{r}^N) = \sum_{i,j>i=1}^{N} \epsilon(\sigma/|\mathbf{r}_i - \mathbf{r}_j|)^n$, where $\mathbf{r}^N = \{\mathbf{r}_1, \mathbf{r}_2, \ldots, \mathbf{r}_N\}$ with $\mathbf{r}_i$ the coordinates of particle i, and ϵ and σ fix the energy and length scales, respectively.

The self-similar nature of the soft-sphere potential has the remarkable property that uniform scaling of particle coordinates does not produce changes the topology of the potential energy landscape, since $E(\lambda \mathbf{r}^N) = \lambda^{-n} E(\mathbf{r}^N)$ [30,31]. In the PEL formalism this scaling property implies that the total number of inherent structures and basins is invariant to volume changes [8,29–31]. The scaling has two important additional consequences which we exploit in the present study.

(i) An isotropic compression of a configuration which is a local potential energy minimum remains a local minimum; the potential energy change associated with the compression coincides with the change in the $E_{\rm IS}$ value [see Fig. 1(b)]. Note that, in general, the isotropic compression of a local minimum configuration does not generate a new local minimum configuration and hence the potential energy change does not coincides with the change of the $E_{\rm IS}$ energy [32].

(ii) An isotropic compression moves the soft-sphere system along a path of constant configurational entropy (since the number of basins of depth $E_{\rm IS}$ at volume V is identical to the number of basins of depth $E_{\rm IS} + \delta E_{\rm IS}$ at volume $V + \delta V$). Because, from a mechanical point of view, P_{IS} is the measure of the change of system's energy under a compression of an IS configuration, these two considerations allow us to write $P_{\rm IS}$ as the volume derivative of the inherent structure energy along a constant configurational entropy path

$$P_{\rm IS}(V,E_{\rm IS}) = -\left(\frac{\partial E_{\rm IS}}{\partial V}\right)_{S_{\rm conf}}. \tag{10}$$

This expression, whose derivation has been based only on the self-similar nature of the soft-sphere potential, coincides with the general expression in Eq. (9) derived from the out-of-equilibrium thermodynamic approach and provides a strong validation of the proposed Eqs. (1) and (2).

To the extent that the out-of-equilibrium formalism is an appropriate description of systems beyond soft spheres, the expression for the inherent structure pressure given by Eq. (9) is quite general. Encouraging support for this statement is given by the behavior of the inherent structure pressure below an ideal glass transition [33].

To summarize, the present paper provides support for the recently proposed out-of-equilibrium approach to supercooled liquids and its corresponding definition of configurational temperature (i.e., the temperature characterizing a system's sampling of inherent structures which are distinct from those it would sample in equilibrium.) In the context of the soft-sphere system, this nonequilibrium formalism provides a consistent expression for the inherent structure pressure $P_{\rm IS}$. Furthermore, the results presented in this paper provide a formal and general derivation of $P_{\rm IS}$ [Eq. (9)] in terms of statistical properties of the landscape [18,8] and open the way for a consistent formulation of thermodynamic properties in disordered materials based on a separation of configurational and vibrational properties.

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