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Equilibrium and out-of-equilibrium thermodynamics in supercooled liquids and glasses

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Abstract
We review the inherent structure thermodynamical formalism and the formulation of an equation of state (EOS) for liquids in equilibrium based on the (volume) derivatives of the statistical properties of the potential energy surface. We also show that, under the hypothesis that during ageing the system explores states associated with equilibrium configurations, it is possible to generalize the proposed EOS to out-of-equilibrium (OOE) conditions. The proposed formulation is based on the introduction of one additional parameter which, in the chosen thermodynamic formalism, can be chosen as the local minimum where the slowly relaxing OOE liquid is trapped.

1. Introduction

The possibility of a consistent description of the thermodynamics of equilibrium and out-of-equilibrium (OOE) (glass) supercooled liquids has been and is an important research direction [1–10]. In recent years, the inherent structure (IS) formalism of Stillinger and Weber [11] has significantly contributed to the understanding of the physics of supercooled liquids and appears to offer a powerful and simple approach for developing a thermodynamics of OOE states. Indeed, on one hand, the IS formalism provides a transparent way to write the partition function in terms of the 'basis' of the local minima (IS) of the underlying potential energy landscape (PEL). On the other hand, state-of-the-art computer simulations provide the possibility of a statistically complete sampling of the PEL explored in equilibrium conditions over a wide temperature range. The numerical analysis of configurations extracted from the canonical ensemble allows us to calculate the energy depth of the ISs explored during the dynamical evolution, to characterize the volumes of their basins of attraction, and to give estimates of their degeneracy (configurational entropy). Eventually it allows us to directly estimate the free energy of the system in terms of landscape properties.

Recently [9] it has been shown that it is possible to write down a model equation of state (EOS) [12] expressed only in terms of quantities describing the statistical properties of the PEL. The crucial step in this process is the evaluation/modelling of the volume dependence of the number of basins, of their energy distribution, and of their volume. The landscape-based PEL EOS is able to predict the thermodynamics of the system in equilibrium [9] and, even more interestingly, OOE [10]—when the ageing system explores states related to equilibrium configurations.

Although the calculations that we have explicitly performed deal with the simulation of the Lewis and Wahnström (LW) model for the fragile molecular liquid orthoterphenyl (OTP) [13, 14], our results are general. Here we review and discuss some general implications of our results for the understanding of the thermodynamics of supercooled liquids and glasses.

2. The constant-volume free energy

In pioneering papers [11], Stillinger and Weber have shown that the partition function $\mathcal{Z}(T)$ at constant volume V can be written as

$$\mathcal{Z}(T) = \int \mathrm{d}e_{IS}\, \Omega(e_{IS}) \mathrm{e}^{-\beta e_{IS}} \mathrm{e}^{-\beta F_{vib}(e_{IS},T)}, \tag{1}$$

where $\beta = 1/k_B T$, e_{IS} is the depth of the local potential energy minimum (IS) of the PEL, $\Omega(e_{IS})\, \mathrm{d}e_{IS}$ is the number of potential energy minima with energy between e_{IS} and $e_{IS} + \mathrm{d}e_{IS}$, and $F_{vib}(e_{IS}, T)$ describes the free energy of the system constrained in one of the basins of depth e_{IS}, averaged over all basins of depth e_{IS}. Following Stillinger and Weber [11], a basin is defined as the set of points in configuration space which lead to the same local minimum under a steepest-descent path. The power of this formulation relies on the fact that the procedures used to associate with each system configuration the corresponding IS are operationally well defined through constant-volume minimization techniques. Numerical evaluation of the density of states in the local minimum allows us to calculate the harmonic contribution to the basin free energy. Starting from equation (1), the free energy of the system can be written as

$$F(T) = \langle e_{IS}(T)\rangle - T S_{conf}(\langle e_{IS}(T)\rangle) + F_{vib}(T, \langle e_{IS}(T)\rangle); \tag{2}$$

here $\langle e_{IS}(T)\rangle$ is the solution to the saddle point approximation to equation (1), and $S_{conf} = k_B \ln(\Omega(e_{IS}))$ is the configurational entropy. F_{vib}, the intrabasin vibrational free energy, is usually written in the harmonic approximation as $F_{vib} = k_B T \langle \sum_{i=1}^{M} \ln(\beta\hbar\omega_i(e_{IS})\rangle$, where $\omega_i(e_{IS})$ is the ith normal-mode frequency ($i = 1, \ldots, M$)) evaluated at the IS, and $\hbar$ is the Planck constant. The sum of the logarithms of the normal-mode frequencies describes the volume (via the curvature) of the basin of attraction of the IS in the harmonic approximation.

Computer simulation results and theoretical insight [15, 16] provide us with valid models for the two crucial quantities $\Omega(e_{IS})$ and F_{vib}, namely:

$$\Omega(e_{IS})\, \mathrm{d}e_{IS} = \mathrm{e}^{\alpha N} \frac{\mathrm{e}^{-(e_{IS}-E_0)^2/2\sigma^2}}{\sqrt{2\pi\sigma^2}}\, \mathrm{d}e_{IS} \tag{3}$$

$$F_{vib}(e_{IS}, T) = k_B T[(a + b e_{IS}) - \ln(\hbar\beta)]. \tag{4}$$

The hypothesis of a Gaussian landscape is supported by the consideration that, if no correlation length diverges, e_{IS} can be thought of as sum of the IS energies of several independent subsystems. In this case the central limit theorem suggests that, since the variance of the energy distribution in each of these independent subsystem is finite, a Gaussian distribution will describe the distribution of e_{IS}-values [15]. We note that this hypothesis will break down in the very low-energy tail, where differences between the

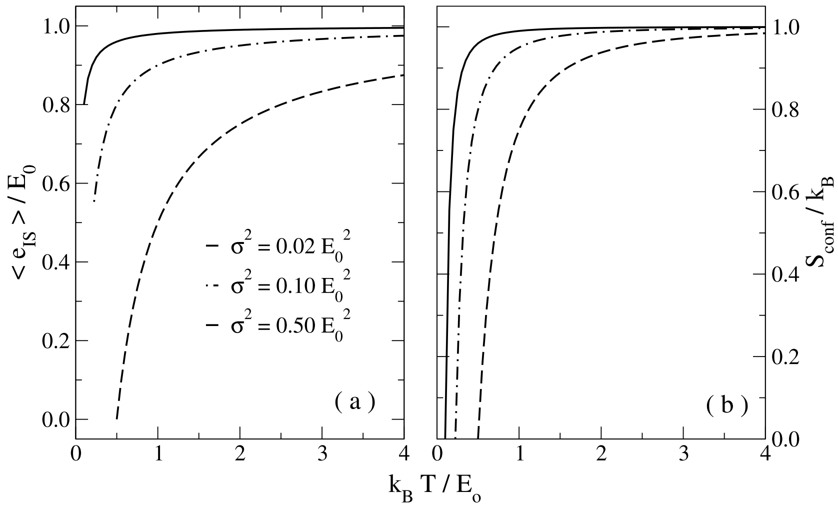

Figure 1. The T-dependence of $\langle e_{IS}\rangle$ (a) and S_{conf} (b) in the approximation of a Gaussian distribution of basin depths and e_{IS}-independence of the basin volume. Curves for $\alpha = 1.0$ and three different values of σ^2/E_0^2 are shown.

Gaussian distribution and the actual distribution become relevant. The second hypothesis ($\sum_{i=1}^{M} \ln(\omega_i(e_{IS})) = a + be_{IS}$) is not crucial, but it is supported by the results of numerical studies.

Substituting in equation (2) and solving, one obtains [16]

$$\langle e_{IS}(T)\rangle = (E_0 - b\sigma^2) - \sigma^2/k_B T \tag{5}$$

$$-T S_{conf}(\langle e_{IS}(T)\rangle) = k_B T\left(\frac{b^2\sigma^2}{2} - \alpha N\right) + b\sigma^2 - \frac{\sigma^2}{2k_B T} \tag{6}$$

$$F_{vib}(T, \langle e_{IS}(T)\rangle) = F_0(E_0, T) - k_B T b\sigma^2(b + \beta). \tag{7}$$

Therefore, $F(T, V)$ is expressed only in terms of proper combinations of the parameters α, E_0, σ, a, and b which are related to the statistical properties of the PEL [9] and to a particular relation between volume and depth of the basins. We also note that from a plot of $\langle e_{IS}\rangle$ versus $1/T$ it is possible to evaluate σ^2 and E_0. A comparison between numerical data and equation (6) allows us to estimate α. In the case where all basins have the same volume ($b = 0$), equations (5) and (6) simplify considerably, and in terms of scaled quantities one obtains

$$\langle e_{IS}(T)\rangle/E_0 = 1 - \frac{\sigma^2/E_0^2}{(k_B T/E_0)} \tag{8}$$

$$S_{conf}(\langle e_{IS}(T)\rangle)/k_B = \alpha - \frac{\sigma^2/E_0^2}{2(k_B T/E_0)^2}. \tag{9}$$

Within the Gaussian approximation, the lowest e_{IS}-value, e_K—characterized by $S_{conf}(e_K) = 0$—is the Kauzman energy:

$$\langle e_K(T_K)\rangle/E_0 = 1 - \sqrt{2\alpha\frac{\sigma^2}{E_0^2}}, \tag{10}$$

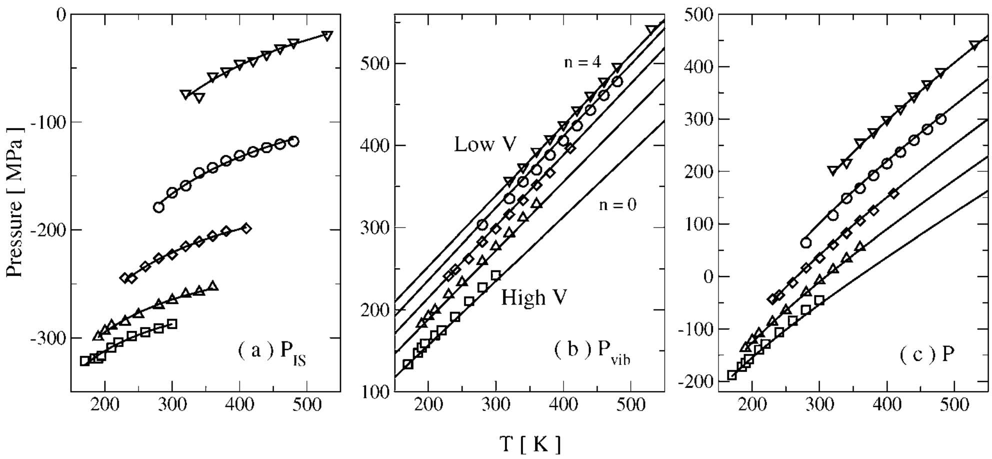

Figure 2. Comparison between the different contributions to the pressure calculated according to the theory (solid curves) and by MD simulations (symbols) for the LW model: (a) IS contribution; (b) vibrational contribution. The curves have been shifted by $n \times 20$ MPa to avoid overlaps. (c) Total pressure. Details on the calculations of these quantities can be found in [9, 10].

and it is reached at a Kauzman temperature T_K given by

$$k_B T_k / E_0 = \sqrt{\frac{(\sigma^2/E_0^2)}{2\alpha}}. \tag{11}$$

The behaviours of $\langle e_{IS} \rangle$ and $S_{conf}(T)$ as functions of T, in reduced units, are shown in figure 1. We note in passing that recent works by Speedy [17] and Sastry [16] have attempted to correlate kinetic fragility with thermodynamic fragility [18], suggesting that σ and α are the statistical properties of the PEL which control the material fragility.

3. Equilibrium equation of state

The generalization of equation (2) to the volume-dependent case requires the determination of the volume dependence of equation (3), i.e., the formulation of an ansatz for the joint probability $\mathcal{P}(e_{IS}, V)$ of finding a value of e_{IS} at a given volume V. We follow the equivalent approach of fitting simultaneously the lhs of equations (4)–(6) determined by MD simulations at different volumes [9]. This procedure allows us to calculate directly the volume dependence of the parameters α, E_0, σ, a, and b introduced above.

Substituting in equation (2) we obtain $F(T, V)$ for the model considered, and the EOS can be finally calculated via $P(T, V) = -\partial_V F(T, V)$ at T constant. From equation (2) it is immediately clear that P can be split into two contributions: a configurational part, P_{conf}, related to the change in the number and depth of available basins with V, and a vibrational part, P_{vib}, related to the change in the volume of the basin with V as

$$P(T, V, e_{IS}) = P_{conf}(V, e_{IS}) + P_{vib}(T, V, e_{IS}). \tag{12}$$

Figure 2 shows the comparison among the MD estimates of the different contributions to the pressure (symbols) and the predictions of the above theory, for the case of the LW model. The excellent agreement between the two sets of data confirms the validity of the procedure introduced above which provides us with an effective EOS for the system under study based on the statistical properties of the landscape as expressed in equations (3) and (4).

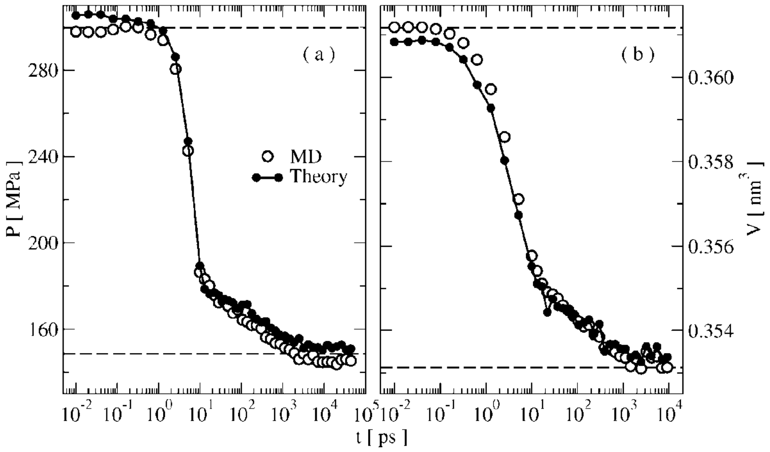

Figure 3. OOE simulation protocols: (a) pressure evolution after a T-jump at constant volume per molecule $V = 0.345$ nm^3 from 480 to 340 K; (b) volume evolution after a P-jump at constant temperature $T = 320$ K from 13.4 to 60.7 MPa. Details can be found in [10]. Dashed lines are the equilibrium values at the initial and final state.

4. Out-of-equilibrium equation of state

The possibility of a proper thermodynamical description of OOE systems has been widely debated [1–3, 19, 20]. In particular it has been recognized that this should be possible by adding one or more history-dependent parameters to the equilibrium EOS. The arguments discussed above allow us to go further in this direction [10]. Indeed the only hypothesis that we made is that equations (3) and (4) are valid. In all the OOE conditions where these two conditions are met, i.e., the (gently) system-driven OOE explores states which are typical at equilibrium, the theory is expected to hold at the expense of adding one parameter to the equilibrium EOS. Looking at equations (4)–(6), the choice of the basin depth e_{IS} as the additional parameter turns out to be very natural.

To the extent of this extension, the validity of equation (12) in OOE conditions is crucial, allowing us to link P_{conf} and P_{vib} to e_{IS} and V. If this is the case, the knowledge of e_{IS} and V is sufficient for calculating both P_{conf}, P_{vib} and their sum P according to equation (12). Similarly, the values of P, T, and e_{IS} are sufficient for predicting V, since both $P_{conf}(e_{IS}, V)$ and $P_{vib}(e_{IS}, T, V)$ can be estimated as functions of V. The predicted V is the value for which $P_{conf}(e_{IS}, V) + P_{vib}(e_{IS}, T, V)$ matches the external (fixed) pressure.

In figure 3 we show the comparison among MD results and the predictions of the OOE EOS for two different OOE protocols via computer simulation. In particular, we consider in figure 3(a) the case of a T-jump at constant volume, and in figure 3(b) a P-jump at constant temperature. In the first case the dynamical evolution of e_{IS} together with the (fixed) values of V and T allow us to predict the dynamical evolution of P; in the second one, the time dependence of e_{IS} together with P and T allow us to predict the evolution of P.

An interesting representation of the ageing processes discussed above is the parametric plot in the P_{IS}–e_{IS} plane. In figure 4 we show the path followed by the ageing system for the two protocols discussed above (figures 4(a) and (b)). Panels (c) and (d) report the comparison between the basin volume described by the quantity $\sum_{i=1}^{M} \ln(\omega_i(e_{IS}))$ during the ageing process and the basin volume of the corresponding basin (same e_{IS} and V) explored in equilibrium conditions. In all cases the agreement between the calculated quantities and the theoretical prediction is quite good, confirming the validity of our approach.

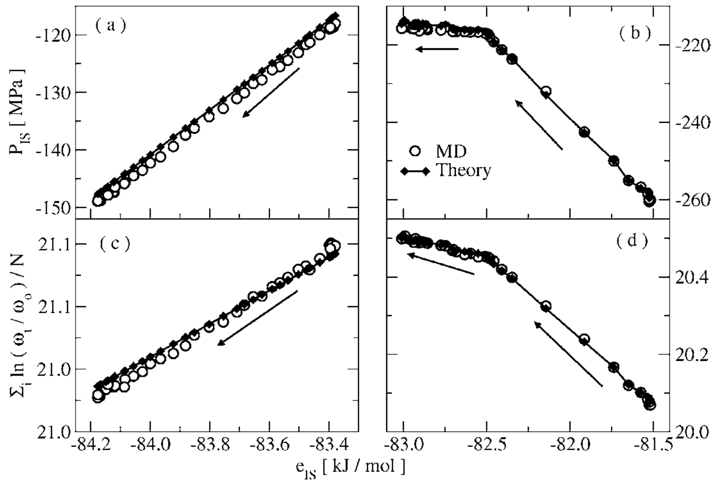

Figure 4. Paths of the ageing process in the P_{IS}–e_{IS} plane for the OOE protocols considered in figure 3: (a) a T-jump at constant pressure; (b) a P-jump at constant temperature. The arrows indicate the time evolution direction. Details can be found in [9, 10]. Panels (c) and (d) report the comparison between the 'basin volume' during the ageing process and the 'basin volume' of the corresponding basin (same e_{IS} and same V) explored in equilibrium conditions. The basin volume is described by $\sum_{i=1}^{M} \ln(\omega_i(e_{IS}))$.

Figure 4(b) is of particular interest, showing that in the OOE dynamics following a pressure jump two different regimes can be recognized. For times shorter than the barostat time constant (see [10] for details) the system responds to the external increase of pressure in a solid-like fashion, i.e., the PEL basins initially populated are only deformed by the volume change. Only for longer times, when the pressure has reached the equilibrium value, does the system start to age among basins different from the original ones.

5. Conclusions

In this paper we have reviewed some recent results on a general approach to the thermodynamics of equilibrium supercooled liquids and glasses [9, 10]. We have discussed how it is possible to formulate an equilibrium EOS in terms of quantities describing the statistical properties of the PEL. These findings allow us to better understand the nature of the different terms contributing to the total pressure of the system, and fill the gap usually found among experiments (usually performed at constant P) and computer simulations (usually performed at constant V).

The generality of the hypothesis that we have introduced allows us to generalize our approach to OOE conditions. In all the cases where the hypotheses introduced are met, i.e., the system ages among states typical at thermodynamical equilibrium, it is possible to write down an OOE EOS at the expense of the addition of one more parameter. This quantity can be naturally chosen as the depth of the explored IS. The correctness of this generalization has been checked under several OOE conditions. Its limits of validity under more severe OOE conditions where more then one additional parameter is needed for a consistent description (like in the so-called Kovacs memory experiments [19–21]) are currently under investigation. We foresee the possibility that, under large variations of the temperature and/or pressure, different parts of the system will age with different speeds producing, as a net result, a material characterized by an e_{IS}-distribution of the component subsystems different from the equilibrium one, and/or a material for which the relation between basin volume and depth is different from that at equilibrium.

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