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 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 aging the system explores states associated to equilibrium configurations, it is possible to generalize the proposed equation of state to out-of-equilibrium 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 minima where the slowly relaxing out-of-equilibrium liquid is trapped.

1. Introduction

The possibility of a consistent description of the thermodynamics of equilibrium and out-of-equilibrium (glass) supercooled liquids has been and it is an important research line [1, 2, 3, 4, 5, 6, 7, 8, 9, 10]. In recent years, the inherent structure (IS) formalism by 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 out-of-equilibrium (OOE) states. Indeed, on one side, the IS formalism provides a transparent way for writing the partition function in terms of the “base” of the local minima (inherent structures) of the underlying potential energy landscape (PEL). On the other side, state of the art computer simulations provide the possibility of a statistically complete sampling of the PEL explored in equilibrium conditions in 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 volume 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 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/modellization of the volume dependence of the number of basins, of their energy distribution and volume. The landscape based PEL-EOS is able to predict the thermodynamics of the
system in equilibrium and, even more interestingly, in out-of-equilibrium—when the aging system explores states related to equilibrium configurations.

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

2. The constant volume free energy

In pioneering papers, Stillinger and Weber have shown that the partition function $Z(T)$ at constant volume can be written as

$$Z(T) = \int de_{IS} \Omega(e_{IS}) e^{-\beta e_{IS}} e^{-\beta F_{vib}(e_{IS}, T)}$$

where $\beta = 1/k_B T$, $e_{IS}$ is the depth of the local potential energy minima (IS) of the PEL, $\Omega(e_{IS}) de_{IS}$ is the number of potential energy minima with energy between $e_{IS}$ and $e_{IS} + de_{IS}$, and $F_{vib}(e_{IS}, T)$ describes the free energy of the system constrained in one of the basin of depth $e_{IS}$, averaged over all basins of depth $e_{IS}$. Following Stillinger and Weber, a basin is defined as the set of points in configuration space which lead to the same local minima under a steepest descent path. The power of this formulation relies in the fact that the procedures used to associate to 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 minima allows us to calculate the harmonic contribution to the basin free energy.

Starting from Eq. (1), the free energy of the system can be written as

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

where $\langle e_{IS}(T) \rangle$ is the solution to the saddle point approximation to Eq. (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

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

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 energy 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. We note that this hypothesis will break down at the very low energy tail, where differences between the gaussian distribution and the actual distribution become relevant. The second hypothesis ($\sum_{i=1}^{M} \ln(\hbar \omega_i(e_{IS})) = a + b e_{IS}$) is not crucial, but it is supported by the results of numerical studies.
Substituting in Eq. (2) and solving, one obtains [16]:

\[
\langle e_{IS}(T) \rangle = \left( E_o - b\sigma^2 \right) - \sigma^2/k_BT \tag{5}
\]

\[-TS_{conf}(\langle e_{IS}(T) \rangle) = k_BT \left( \frac{b^2\sigma^2}{2} - \alpha N \right) + b\sigma^2 - \frac{\sigma^2}{2k_BT} \tag{6}
\]

\[F_{vib}(T, \langle e_{IS}(T) \rangle) = F_o(E_o, T) - k_BT b\sigma^2(b + \beta). \tag{7}\]

Therefore, \(F(T, V)\) is expressed only in terms of proper combinations of the parameters \(\alpha, E_o, \sigma, a, \) 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 \(\langle e_{IS} \rangle vs 1/T\) it is possible to evaluate \(\sigma^2\) and \(E_o\). A comparison between numerical data and Eq. (6) allows us to estimate \(\alpha\). In the case where all basins have the same volume \((b = 0)\), Eqs. (5) and (6) simplify considerably, and in terms of scaled quantities one obtains

\[
\frac{\langle e_{IS}(T) \rangle}{E_o} = 1 - \frac{\sigma^2/E_o^2}{(k_BT/E_o)} \tag{8}
\]

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

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

\[
\frac{\langle e_K(T_K) \rangle}{E_o} = 1 - \sqrt{2\sigma^2/E_o^2}, \tag{10}\]

and it is reached at a Kauzman temperature \(T_K\) given by

\[k_BT_k/E_o = \sqrt{\frac{\sigma^2/E_o^2}{2\alpha}}. \tag{11}\]

The behavior of \(\langle e_{IS} \rangle\) and \(S_{conf}(T)\) as a function of \(T\), in reduced units, is shown in Fig. 1. We note on passing that recent works by Speedy [17] and Sastry [16] have

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**Figure 1.** \(T\)-dependence of \(\langle e_{IS} \rangle\) (a) and \(S_{conf}\) (b) in the approximation of Gaussian distribution of basin depths and \(e_{IS}\)-independence of the basin volume. Curves for \(\alpha = 1.0\) and three different values of \(\sigma^2/E_o^2\) are shown.
attempted to correlate kinetic fragility to thermodynamic fragility [18], suggesting that $\sigma$ and $\alpha$ are the statistical properties of the PEL which control the material fragility.

3. Equilibrium equation of state

The generalization of Eq. (2) to the volume dependent case requires the determination of the volume dependence of Eq. (3), i.e., the formulation of an ansatz for the joint probability $P(e_{IS}, V)$ to find a value of $e_{IS}$ at a given volume $V$. We follow the equivalent approach of fitting simultaneously the l.h.s. of Eqs. (5)(6) and (4) determined by MD simulations at different volumes [9]. This procedure allows us to calculate directly the volume dependence of the parameters $\alpha$, $E_o$, $\sigma$, $a$, and $b$ introduced above.

Substituting in Eq. (2) we obtain $F(T, V)$ for the model considered, and the equation of state can be finally calculated via $P(T, V) = -\partial_V F(T, V)$ at $T$ constant. From Eq. (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

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

Fig. 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 an effective equation of state for the system under study based on the statistical properties of the landscape as expressed in Eqs. (3) and (4).
4. Out of equilibrium equation of state

The possibility of a proper thermodynamical description of out-of-equilibrium systems has been widely debated [1, 2, 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 equation of state. The arguments discussed above allow us to go further in this direction [10]. Indeed the only hypothesis we made is the validity of Eqs. (3) and (4). In all the out-of-equilibrium conditions where these two conditions are met, i.e., the system (gently) driven out of equilibrium explores states which are typical at equilibrium, the theory is expected to hold at the expenses of adding one parameter to the equilibrium EOS. Looking at Eqs. (5)-(6) and (4), 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 Eq. (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 to calculate both $P_{conf}$, $P_{vib}$ and their sum $P$ according to Eq. (12). Similarly, the values of $P$, $T$ and $e_{IS}$ are sufficient to predict $V$, since both $P_{conf}(e_{IS}, V)$ and $P_{vib}(e_{IS}, T, V)$ can be estimated as a function 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 Fig. 3 we show the comparison among MD results and the predictions of the OOE equation of state for two different OOE protocols via computer simulation. In particular, we consider in Fig. 3(a) the case of a T-jump at constant volume, and in Fig. 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 aging processes discussed above is the parametric plot in the $P_{IS} - e_{IS}$ plane. In Fig. 4 we show the path followed by the aging system for the two protocols discussed above (Figs. 3(a) and (b)).

Figure 3. OOE simulation protocols: (a) Pressure evolution after a T-jump at constant volume per molecule $V = 0.345$ nm$^3$ from 480 K to 340 K; (b) Volume evolution after a P-jump at constant temperature $T = 320$ K from 13.4 MPa to 60.7 MPa. Details can be found in Ref. [10].
Figure 4. Paths of the aging process in the $P_{IS} - e_{IS}$ plane for the OOE protocols considered in Fig. 3: (a) $T$-jump at constant pressure; (b) $P$-jump at constant temperature. The arrows indicate the time evolution direction. Details can be found in Refs. [9, 10]. Panels (c) and (d) report the comparison between the "basin volume" during the aging process with the "basin volume" of the corresponding basin (same $e_{IS}$ and same $V$) explored in equilibrium conditions. The basin volume is described by $\sum_{i=1}^{M} \ln(\omega_i(e_{IS}))$.

Panels (c) and (d) report the comparison between the basin volume described by the quantity $\sum_{i=1}^{M} \ln(\beta h\omega_i(e_{IS}))$ during the aging 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.

Fig. 4(b) is of particular interest, showing that in the OOE dynamics following a pressure jump can be recognized two different regimes. For times shorter than the barostat time constant (see Ref. [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, the system starts 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 equation of state in terms of quantities describing the statistical properties of the potential energy landscape. 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 we have introduced, allow us to generalize our approach to out of equilibrium conditions. In all the cases where the introduced hypotheses are met, i.e., the system ages among states typical at thermodynamical equilibrium, it is possible to write down an OOE equation of state at the expenses of the addition of one more parameter. This quantity can be naturally chosen as the depth of the explored inherent structures. 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, 20, 21]) is currently under investigation. We foresee the possibility that, under large variations of the temperature and/or pressure, different part of the system will age with different speed producing, as a net result, a material characterized by a distribution of $e_{IS}$ of the composing subsystems different from the equilibrium one, and/or a material for which the relation between basin volume and depth is different from equilibrium.

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