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Numerical evaluation of the statistical properties of a potential energy landscape

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Abstract

The techniques which allow the numerical evaluation of the statistical properties of the potential energy landscape for models of simple liquids are reviewed and critically discussed. Expressions for the liquid free energy and its vibrational and configurational components are reported. Finally, a possible model for the statistical properties of the landscape, which appears to describe correctly fragile liquids in the region where equilibrium simulations are feasible, is discussed.

1. Introduction

Understanding the dynamic and thermodynamic properties of supercooled liquids is one of the more challenging tasks of condensed matter physics [1–6]. A significant amount of experimental [7–10], numerical [11], and theoretical work [12–16] is being currently devoted to the understanding of the physics of the glass transition and to the associated slowing down of the dynamics. In recent years the study of the topological structure of the potential energy landscape (PEL) [17] and the connection between the properties of the PEL and the dynamical behaviour of glass forming liquids has become an active field of research. Among the thermodynamic formalisms amenable to use in numerical investigation of the PEL properties, a central role is played by the inherent structure (IS) formalism introduced by Stillinger and Weber [17]. Properties of the PEL, such as depth, number, and shape of the basins of the potential energy surface are calculated and used in the evaluation of the liquid free energy in the supercooled state [18–21]. In the IS formalism, the system free energy is expressed as a sum of an entropic contribution, accounting for the number of explored basins, and a vibrational contribution, expressing the free energy of the system when constrained in one of the basins [17].

In this work we review the numerical techniques which allow the evaluation of the statistical properties of the PEL for atomic and molecular systems [18, 19, 21–24]. The paper is organized as follows. Section 2 provides a brief introduction to the IS formalism, introduced by Stillinger and Weber [17]. Within this formalism, an exact expression for the liquid free energy, based on landscape properties, can be derived. Section 3 reviews the numerical techniques which allow a precise numerical evaluation of the liquid free energy. Section 4 describes the numerical techniques required for the evaluation of the IS energies. Section 5 discusses techniques for evaluating the vibrational component of the free energy. Section 6 shows how, from the previous information, is possible to evaluate the configurational entropy. Section 7 discusses a possible modelling of the statistical properties of the landscape, based on the hypothesis of a Gaussian distribution of the basin's depth [19, 21, 25], and compares the predictions of the model with numerical results for a molecular system.

2. The free energy in the IS formalism

In the IS formalism [17], the free energy of a supercooled liquid is expressed in terms of the statistical properties of the PEL. The potential energy surface is partitioned into so-called basins, each defined as the set of points such that a steepest descent path ends in the same local minimum. The configuration at the minimum is called the IS and its energy and pressure are usually indicated as e_{IS} and P_{IS}. The partition function can be expressed as a sum of the Boltzmann weight over all the basins, i.e., as a sum over the basin partition functions. As a result, the Helmholtz liquid free energy $F(T, V)$ can be written as [17]

$$F(T,V) = \langle e_{IS}(T,V)\rangle - TS_{conf}(T,V) + f_{vib}(T,V), \qquad (1)$$

where

- $\langle e_{IS}\rangle$ is the average energy of the local minima explored at temperature T and volume V;
- f_{vib} is the vibrational free energy, i.e., the free energy of the system constrained in one basin, a quantity depending on the shape of the basins explored;
- S_{conf} is the configurational entropy, which counts the number of basins explored.

The numerical evaluation of $F(T, V)$, $\langle e_{IS}(T, V)\rangle$, and $f_{vib}(T, V)$ is sufficient for calculating S_{conf} and, from it, the number of basins $\Omega(e_{IS})\,\mathrm{d}e_{IS}$ with depth between e_{IS} and $e_{IS} + \mathrm{d}e_{IS}$. Indeed, in the thermodynamic limit, $\ln\Omega(e_{IS})$ can be derived from a plot of S_{conf} versus $\langle e_{IS}\rangle$ (parametric in T). This quantity, together with the $\langle e_{IS}\rangle$ dependence of f_{vib}, provides a precise quantification of the statistical properties of the landscape.

3. Numerical evaluation of $F(T, V)$

This section describes the numerical techniques used to evaluate the liquid free energy, based on thermodynamic integration [18, 19, 21, 22, 26]. First, a path in the (T, V) plane, connecting the ideal gas state to the desired state point, has to be selected. The selected path must avoid the liquid–gas first-order line. A convenient choice is a constant-temperature path (with $T = T_0$ higher than the liquid–gas critical temperature) from infinite volume to the desired volume, followed by a constant-volume path from T_0 down to the range of temperature of interest.

In the general case of a system of N rigid molecules, the ideal gas free energy is

$$F_{ig}(T,V,N) = -Nk_BT\left\{1 + \frac{1}{2}\ln\pi - \ln\nu + \ln\left[\frac{V\sqrt{\mathcal{A}^3\mathcal{R}_x\mathcal{R}_y\mathcal{R}_z}}{N}T^3\right]\right\}, \qquad (2)$$

where $\mathcal{A} \equiv 2\pi m k_B/h^2$, $\mathcal{R}_\mu \equiv 8\pi^2 k_B I_\mu/h^2$ (with μ denoting x, y, or z), I_μ is the inertia moment of the molecule with respect the axis μ, and $\ln \nu$ accounts for the molecular symmetry. In the case of C_{2v} molecules (such as water), $\nu = 2$, due to there being two possible degenerate angular orientations of the molecule [27].

To perform the thermodynamics integration along the isotherm T_0, one needs to select about 20–30 state points at different volumes (figure 1(a)). Of course, the smallest volume chosen must coincide with the final volume V_0. The largest V-value (V_∞) must be chosen in such a way that the vast majority of the molecular interactions are binary collisions, i.e., such that the volume dependence of the pressure is well described by the (first-order) virial expansion. At large volumes, although the dynamics is very fast, care has to be taken to run the simulation for long enough to sample a large number of binary collisions.

The free energy at (T_0, V_0) can be calculated as

$$F(T_0, V_0) = F_{ig}(T_0, V_0) - \int_\infty^{V_0} \mathrm{d}V\, P_{ex}(T_0, V) + \frac{U(T_0, V_0)}{T_0}, \tag{3}$$

where $U(T_0, V_0)$ is the potential energy and $P_{ex}(T_0, V)$ is the excess pressure, i.e., the pressure in excess of the ideal gas pressure. The calculated $P_{ex}(T_0, V)$ curve can be fitted according to the polynomial in powers of V^{-1} (figure 1(b)):

$$P_{ex}(T_0, V) = \sum_{k=1}^{n} a_k(T_0) V^{-(k+1)}, \tag{4}$$

giving

$$F(T_0, V_0) = F_{ig}(T_0, V_0) + \sum_{k=1}^{n} \frac{a_k(T_0) V_0^{-k}}{k} + \frac{U(T_0, V_0)}{T_0}. \tag{5}$$

To perform the thermodynamic integration along a constant-V_0 path, it is necessary to evaluate the internal energy $U(T, V_0)$ as a function of T, from T_0 down to the lowest state where equilibration of the system is feasible (figure 1(c)). The resulting free energy $F(T, V_0)$ can be calculated as

$$F(T, V_0) = F(T_0, V_0) + 3R \ln(T/T_0) + \int_{T_0}^{T} \frac{\mathrm{d}T}{T} \frac{\partial U(T, V_0)}{\partial T}. \tag{6}$$

The $3R \ln(T/T_0)$ term accounts for the ideal gas contribution to the free energy. Again, a fit of $U(T, V_0)$ versus T is required to evaluate the integral in the above expression. One possibility, which has been often found to be very successful for dense systems (small V_0) [22, 26], is to fit $U(T, V_0)$ versus T according to the Tarazona law [28], i.e., $U(T, V_0) = b_0(V_0) + b_1(V_0)T^{3/5}$. Of course, for the present purposes, any functional form which correctly represents $U(T, V_0)$ can be selected.

In summary, performing thermodynamic integration, an accurate numerical expression for $F(V, T)$ can be obtained.

4. The average IS energy $\langle e_{IS} \rangle$

This section describes how to calculate the average IS energy $\langle e_{IS}(T, V) \rangle$. Recently, it has been shown that, for cooling at constant volume, on entering the supercooled region, the system starts to explore basins of lower and lower e_{IS} [32]. The T-dependence of the average explored basin depth follows a T^{-1}-law [19, 21, 23, 33] for fragile liquids. Note that for silica, the prototype of a strong liquid, the T^{-1}-law is not observed and $\langle e_{IS}(T, V) \rangle$ appears to approach a constant value on cooling [20].

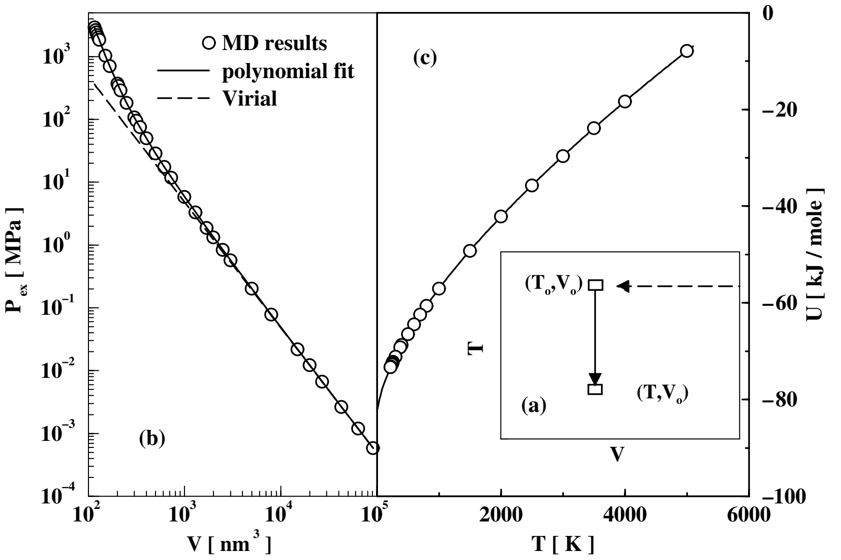

Figure 1. (a) Thermodynamic integration paths used to calculate the total free energy at the thermodynamical points of interest, starting from the ideal—non-interacting—gas state. (b) Excess pressure at $T = T_0$ as a function of volume. The open circles are the MD results. The dashed line is the first term of the virial expansion for the excess pressure; the solid curve is a third-order polynomial fit to the entire set of data. (c) The potential energy (open circles) at the volume V_0 over the entire temperature range considered; the solid curve is the fit of the data. The data are from our simulation [21] of a system of $N = 343$ molecules modelled by the Lewis and Wahnström model for orthoterphenyl [29], whose dynamics [30] and thermodynamics [21, 31] features have been studied in detail.

In order to evaluate $\langle e_{IS}(T, V)\rangle$, one needs to perform steepest descent potential energy minimizations for a statistically representative ensemble of equilibrium configurations, to locate their corresponding IS, i.e., local minima. For efficiency reasons, the search for the closest local minima is performed using the conjugate gradient algorithm [34]. In this algorithm, the system evolves along a sequence of straight directions until the minimum is reached. In each step, the new search direction recalls the directions already explored, improving the algorithm efficiency. In rigid molecule systems, each step is composed via a sequence of minimizations of the centre of mass coordinates, followed by a minimization of the angular coordinates. Rotations around the principal axis of the molecule are often chosen. The minimization procedure is continued until the energy changes by less than a preselected precision. Since the change in $\langle e_{IS}(T)\rangle$ in supercooled states is often less than one per cent of its own value, a high precision is required in the minimization procedure.

In figure 2 we show $\langle e_{IS}\rangle$ (a) as a function of T and (b) as a function of $1/T$ for a rigid molecular model.

5. The vibrational free energy

The vibrational free energy $f_{vib}(e_{IS}, T, V) = U_{vib}(e_{IS}, T, V) - TS_{vib}(e_{IS}, T, V)$ is the free energy associated to the exploration of a basin of depth e_{IS} at temperature T and volume V. $f_{vib}(e_{IS}, T, V)$ takes into account both the kinetic energy of the system and the local structure

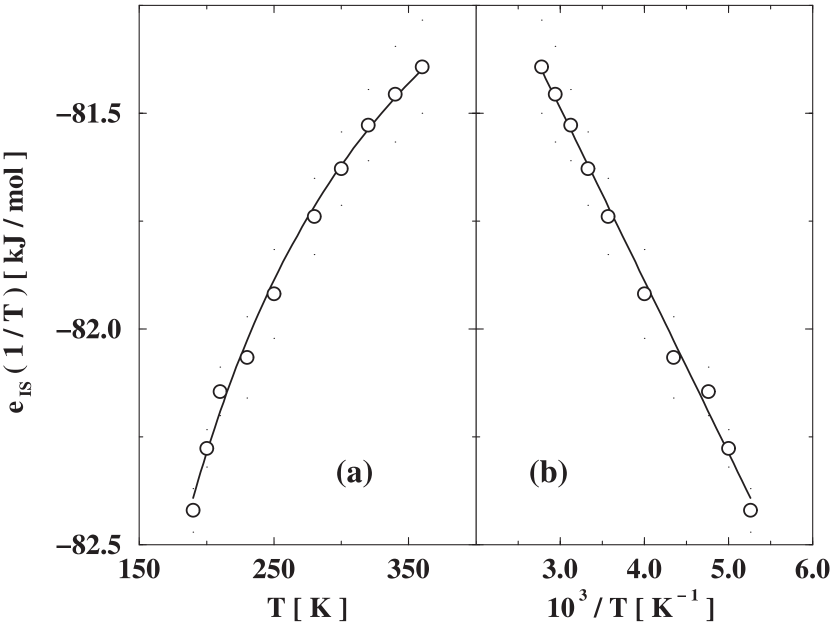

Figure 2. $\langle e_{IS} \rangle$ as a function of T (a) and as a function of $1/T$ (b). The data are from simulations [21] of a system $N = 343$ molecules modelled by the Lewis and Wahnström model for orthoterphenyl [29].

of the basin with energy e_{IS}. From a formal point of view, it is defined as

$$f_{vib}(e_{IS}, T, V) = -k_B T \ln\left(\frac{\Lambda_x \Lambda_y \Lambda_z}{\lambda^{3N}} \sum{}' \frac{\int_{V_{basin}} \exp(-\beta[V(\boldsymbol{r}^N) - e_{IS}])\, \mathrm{d}\boldsymbol{r}^N}{\Omega(e_{IS})\, \mathrm{d}e_{IS}} \right), \qquad (7)$$

where $\sum'$ is the sum over all the basins with energy depth e_{IS}. The integration of the Boltzmann factor is performed over all points in configuration space associated with the selected basin. Here $\Lambda_\mu \equiv (2\pi I_\mu k_B T)^{1/2}/h$, $\lambda \equiv h(2\pi m k_B T)^{-1/2}$ is the de Broglie wavelength, and $V(\boldsymbol{r}^N)$ is the potential energy.

The evaluation of the integral requires the exact knowledge of the shape of the PEL in the basin and, in general, it will give rise to a complex T-dependence of the vibrational energy. The best that can be done at the present time is to assume that the e_{IS}-dependence in f_{vib} is captured by the e_{IS}-dependence of the density of states of the basin, evaluated at the IS configuration [21, 31]. In other words, the vibrational free energy is split into a harmonic contribution (which depends on the curvature of the potential energy at the minimum) and an anharmonic contribution, which is often assumed basin independent. In molecular systems, the Hessian, the matrix of the second derivatives of the potential energy, is calculated numerically, selecting as molecular coordinates the centre of mass and the angles associated with the rotations around the three principal molecular inertia axes. Diagonalization is performed with standard numerical routines.

In the harmonic approximation, the free energy associated with a single oscillator at frequency ω is $k_B T \ln(\beta\hbar\omega)$. Hence, the basin free energy can be written as

$$f_{vib}(e_{IS}, T, V) = k_B T \left\langle \sum_{i=1}^{6N-3} \ln(\beta\hbar\omega_i(e_{IS})) \right\rangle' + F_{anh}(T, V), \qquad (8)$$

with

$$U_{vib}(T, V) = (6N-3)\frac{k_B T}{2} + U_{anh}(T, V), \tag{9}$$

and

$$S_{vib}(e_{IS}, T, V) = \left\langle \sum_{i=1}^{6N-3} \left(1 - \ln\left[\frac{\hbar\omega_i(e_{IS})}{k_B T}\right]\right)\right\rangle' + S_{anh}(T, V); \tag{10}$$

here the $\omega_i(e_{IS})$ are the frequencies of the $6N-3$ independent harmonic oscillators given by the square roots of the $6N-3$ non-zero eigenvalues of the Hessian matrix evaluated in the IS. $\langle\ \rangle'$ is the average over all the basins with the same energy e_{IS}. Note that the above equations are derived assuming

$$\left\langle \sum_{i=1}^{6N-3} \ln(\beta\hbar\omega_i(e_{IS}))\right\rangle' = \ln\left\langle \exp\left(\sum_{i=1}^{6N-3} \ln(\beta\hbar\omega_i(e_{IS}))\right)\right\rangle'. \tag{11}$$

For the molecular systems studied so far, this approximation introduces an error smaller than 1%. The relevant approximation consists in dropping the e_{IS}-dependence in the anharmonic contribution to the vibrational free energy F_{anh} (and of course in $U_{anh}(T, V)$ and $S_{anh}(T, V)$). In other words, the anharmonicities are assumed to be identical in all basins. Under such an approximation, $U_{anh}(T, V)$ can be calculated from the simulation data as

$$U_{anh}(T, V) = U(T, V) - \langle e_{IS}(T, V)\rangle - (6N-3)\frac{k_B T}{2}, \tag{12}$$

and it can be well fitted by an expansion in powers of T, starting from T^2, as

$$U_{anh}(T, V) = \sum_{k=2}^{N_c} c_k(V) T^k. \tag{13}$$

Correspondingly, $S_{anh}(T, V)$ can be estimated by thermodynamic integration along the isochore between temperatures 0 and T as

$$S_{anh}(T, V) = \int_0^T \frac{\mathrm{d}T'}{T'} \frac{\partial U(T, V)}{\partial T} = \sum_{k=2}^{N_c} \frac{k c_k(V)}{k-1} T^{k-1}. \tag{14}$$

An alternative method for estimating the anharmonicities of the system is to assume that all the basins are quasi-harmonic and that the T-dependence of $U_{anh}(T, V)$ arises from the e_{IS}-dependence of the anharmonicity, i.e.

$$U_{anh}(T, V) = D(e_{IS}) T^2, \tag{15}$$

and

$$S_{anh} = -2D(e_{IS}) T^2. \tag{16}$$

$D(e_{IS})$ can be calculated from a parametric plot of $U_{anh}(T, V)/T^2$ versus e_{IS}.

By incorporating the anharmonic corrections, which in the models of simple fragile liquids studied so far are not particularly significant [21, 22], a good estimate of the basin free energy is obtained. We note on passing that for the cases of network forming liquids, anharmonic corrections are relevant [20, 23] and must be taken into account.

In the assumption of $U_{anh}(T, V)$ independent of e_{IS}, all the e_{IS}-dependence in the basin free energy is carried by the term $\mathcal{V}(V, e_{IS}) \equiv \langle\sum_{i=1}^{6N-3} \ln\omega_i(e_{IS})\rangle$. A parametrization of such quantity as a function of e_{IS} allows one to simply connect the basin free energy to the basin depth. Although in all models studied so far [19, 21, 31, 35] a linear relation between basin depth and 'basin shape' $\mathcal{V}$ satisfactorily describes their relation, here we use the more general expression

$$\mathcal{V} = a(V) + b(V) e_{IS} + c(V) e_{IS}^2, \tag{17}$$

which best describes the simulation data (figure 3(a)).

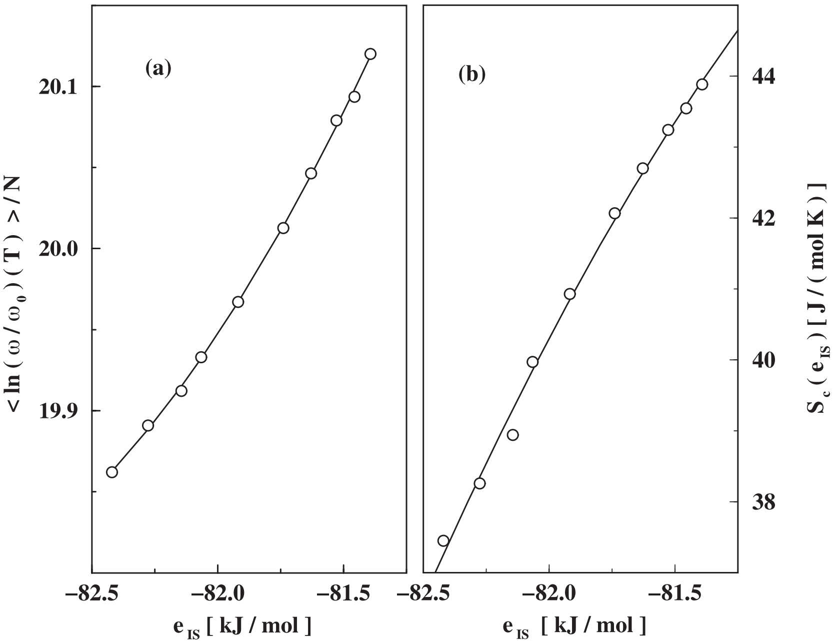

Figure 3. $\mathcal{V}$ (a) and S_{conf} (b) as a function of e_{IS}.

6. The statistical properties of the landscape

In the previous section we have discussed how to relate the basin shape to the basin depth. In this section, we exploit the formulation of the liquid free energy in the IS formalism to evaluate the number of PEL basins as a function of the basin depth.

This quantity is of primary interest both for comparing with the recent theoretical calculations [15, 26] and for examining some of the proposed relations between dynamics and thermodynamics [16, 36, 37] connecting a purely dynamical quantity such as the diffusion coefficient to a purely thermodynamical quantity (S_{conf}). The number of basins Ω as a function of the basin depth e_{IS} has been recently evaluated for a few models [18–24, 38], and from the analysis of experimental data [39–41]. $S_{conf}(T, V)$—the logarithm of the number of basins explored—can be calculated as the difference of the entropic parts of equations (6) and (10), i.e., as

$$S_{conf}(T, V) = S(T, V) - S_{vib}(T, V) - S_{anh}(T, V). \tag{18}$$

In the thermodynamic limit, when fluctuations are negligible, a parametric plot in T of $S_{conf}(T, V)/k_B$ versus $\langle e_{IS}(T, V)\rangle$ provides an accurate estimate of the number of basins of depth e_{IS}. This information, together with the information on the e_{IS}-dependence of the basin shape (or volume) (equation (17)), completely defines the statistical properties of the landscape, at least in the range of e_{IS}-values sampled by the system in the T-region studied. The availability of $S_{conf}(e_{IS})$ (figure 3(b)) and $\mathcal{V}(e_{IS})$ (figure 3(a)) opens the possibility of a modelling of the thermodynamic of the system in terms of landscape properties, as discussed in the next section.

7. The random energy model: the Gaussian landscape

A modelling of the statistical properties of the landscape is the next conceptual step in the development of a thermodynamic description of the liquid in the IS formalism. A possible modelling, which appears to be consistent with the numerical evidence for fragile liquids, is based on the hypothesis that the number $\Omega(e_{IS})\,\mathrm{d}e_{IS}$ of distinct basins of depth between e_{IS} and $e_{IS}+\mathrm{d}e_{IS}$ in a system of N atoms or molecules is described by a Gaussian distribution [19, 23, 25, 31, 42], i.e.,

$$\Omega(e_{IS})\,\mathrm{d}e_{IS} = \mathrm{e}^{\alpha N}\frac{\mathrm{e}^{-(e_{IS}-E_0)^2/2\sigma^2}}{(2\pi\sigma^2)^{1/2}}\,\mathrm{d}e_{IS}. \tag{19}$$

Here the amplitude $\mathrm{e}^{\alpha N}$ accounts for the total number of basins, E_0 has the role of an energy scale, and σ^2 measures the width of the distribution. One can understand the origin of such a distribution by invoking the central limit theorem. Indeed, in the absence of a diverging correlation length, in the thermodynamic limit, each IS can be decomposed into a sum of independent subsystems, each of them characterized by its own value of e_{IS}. The system IS energy, in this case, will be distributed according to equation (19). We note that this hypothesis will break down in the very low-energy tail, where differences between the Gaussian distribution and the actual distribution become relevant. As discussed in [25], the system Gaussian behaviour reflects also some properties of the independent subsystems.

Within the assumptions of equation (19)—Gaussian distribution of basin depths—and of the quadratic dependence of the basin free energy on e_{IS}, both of the harmonic term (equation (17)) and of the anharmonic contribution (i.e. $D(e_{IS}) = d_0 + d_1 e_{IS} + d_2 e_{IS}^2$), an exact evaluation of the partition function can be carried out. The corresponding Helmholtz free energy is given by

$$\begin{aligned} F(T,V) = {} & -TS_{conf}(T,V) + \langle e_{IS}(T,V)\rangle + f_{vib}(E_0,T) \\ & + k_B T\left(b(V) - \frac{d_1(V)T}{k_B}\right)(\langle e_{IS}(T,V)\rangle - E_0) \\ & + k_B T\left(c(V) - \frac{d_2(V)T}{k_B}\right)(\langle e_{IS}(T,V)\rangle^2 - E_0^2). \end{aligned} \tag{20}$$

Moreover, using the notation $B_1 = b(V) - d_1(V)T/k_B$ and $B_2 = c(V) - d_2(V)T/k_B$ we have

$$\langle e_{IS}(T)\rangle = \frac{(E_0(V) - (B_1(V)+\beta)\sigma^2(V))}{1 + 2B_2(V)\sigma^2(V)}, \tag{21}$$

and

$$S_{conf}(T)/k_B = \alpha(V)N - (\langle e_{IS}(T,V)\rangle - E_0(V))^2/2\sigma^2(V). \tag{22}$$

Note that, when we can neglect the anharmonic contributions to $F(T,V)$ and the quadratic term of equation (17), from a plot of $\langle e_{IS}(T)\rangle$ versus $1/T$, one can immediately evaluate two of the parameters of the Gaussian distribution, σ^2 (from the slope) and E_0 (from the intercept). Similarly, from fitting $S_{conf}(T)$ according to equation (22), one can evaluate the last parameter α (see figure 3).

The fitting parameters $\alpha(V)$, $E_0(V)$, and $\sigma^2(V)$ depend in general on the volume. A study of the volume dependence of these parameters, associated with the V-dependence of the shape indicators (a and b in equation (17)) provides a full characterization of the volume dependence of the landscape properties of a model, and offers the possibility of developing a full equation of state based on statistical properties of the landscape.

When comparing numerical simulation data and theoretical predictions—equations (21) and (22)—the range of temperatures must be chosen with great care. Indeed, at high T, the harmonic approximation will overestimate the volume in configuration space associated with an IS. While in harmonic approximation such a quantity is unbounded, the real basin volume is not. Indeed, the sum of all basin volumes is equal to the volume of the system in configuration space. Anharmonic corrections, if properly handled, should compensate for such overestimation, but at the present time no model has been developed that correctly describes the high-T limit of the anharmonic component. Numerical studies have shown that the range of validity of the present estimates of the anharmonic correction does not extend beyond the temperatures at which the system already shows a clear two-step relaxation behaviour in the dynamics. Indeed, the presence of a two-step relaxation is a signature of the system spending a time larger than the microscopic characteristic times around a well defined local minimum.

8. Conclusions

In this paper we have discussed the numerical techniques employed to evaluate the statistical properties of the PEL for molecular systems. These numerical calculations are limited to the region of temperatures and volumes where equilibrium configurations can be numerically generated. Still, very simple arguments can be presented which allow one to generalize the results and formulate a full thermodynamic description of the supercooled liquid state, just in terms of the statistical properties of the PEL.

The possibility of partitioning the free energy and its thermodynamic derivatives as a sum of configurational and vibrational degrees of freedom has been recently exploited to derive a satisfactory description of the equation of state [31, 43] for supercooled liquids just in terms of PEL properties. A better understanding of the nature of each contribution (configurational and vibrational) to quantities such as the total pressure of the system is achieved. At the same time, the availability of detailed estimates for the landscape properties strongly suggests a generalization of this approach to out-of-equilibrium conditions. It has been recently shown [44] that if the system ages exploring the same basins as were visited in equilibrium, it is possible to give an out-of-equilibrium equation of state expressing P not only as a function of V and T but also as a function of the (time-dependent) depth of the basin explored.

The availability of numerical estimates for the statistical properties of the PEL in models of simple liquids should encourage theoreticians to develop schemes for the analytic evaluation of these quantities. If this goal were reached, the understanding of the thermodynamics of supercooled liquids and glasses would be improved significantly.

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