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.

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1. Introduction

Understanding the dynamic and thermodynamic properties of supercooled liquids is one of the more challenging tasks of condensed matter physics ([1, 2, 3, 4, 5, 6]). A significant amount of experimental ([7, 8, 9, 10]), numerical ([11]), and theoretical work ([12, 13, 14, 15, 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 the latest years the study of the topological structure of the potential landscape (PEL) ([17]) and the connection between the properties of the PEL and the dynamical behavior of glass forming liquids has become an active field of research. Among the thermodynamic formalisms amenable to 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 potential energy landscape, 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 supercooled state ([18, 19, 20, 21]). In the IS formalism, the system free energy is expressed as a sum of an entropic contribution, accounting for the number of the explored basins, and a vibrational contribution, expressing the free energy of the system when constrained in one of the basins ([17]).

In this manuscript we review the numerical techniques which allow the evaluation of the statistical properties of the PEL for atomic and molecular systems ([22, 18, 19, 23, 24, 21]). The paper is organized as follow: Sec. 3 provides a brief introduction to the inherent structure 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. Sec. 4 reviews the numerical techniques which allow a precise numerical
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evaluation of the liquid free energy. Sec. 2 describes the numerical techniques requested for the evaluation of the inherent structure energies. Sec. 3 discusses techniques to evaluate the vibrational component of the free energy. Sec. 4 shows how, from the previous information, is possible to evaluate the configurational entropy. Sec. 5 discusses a possible modelization of the statistical properties of the landscape, based on the hypothesis of a gaussian distribution of basin’s depth [25, 19, 21], 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 potential energy landscape (PEL). The potential energy surface is partitioned in so-called basins, 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 inherent structure (IS) and its energy and pressure are usually indicated as $e_{IS}$ and $P_{IS}$. The partition function can be expressed as sum of the Boltzmann weight over all the basins, i.e., as sum over the basin partition functions.

As a result, the Helmholtz liquid free energy $F(T, V)$ can be written as [17]:

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

(1)

where

- $\langle e_{IS} \rangle$ is the average energy of the explored local minima 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 explored basins;
- $S_{conf}$ is the configurational entropy, that counts the number of explored basins.

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 $\Omega(e_{IS})$ with depth between $e_{IS}$ and $e_{IS} + de_{IS}$. Indeed, in the thermodynamic limit, $\ln \Omega(e_{IS})$ can be derived from a plot of $S_{conf}$ vs $\langle e_{IS} \rangle$ (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 [22, 24, 18, 19, 21]. 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 $T = T_o$ higher than the liquid-gas critical temperature) from infinite volume to the desired volume, followed by a constant volume path from $T_o$ 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

$$F_{ig}(T, V, N) = -Nk_BT \left\{ 1 + \frac{1}{2} \ln \pi - \ln \nu + \ln \left( \frac{V \sqrt{A^{3}R_xR_yR_z}}{N} T^3 \right) \right\},$$

(2)

where $A \equiv \frac{2\pi m k_B}{h^2}$, $R_\mu \equiv \frac{\pi^2 k_B T}{h^2}$ – with $\mu$ denoting $x$, $y$, or $z$ --, $I_\mu$ is the inertia moment of the molecule with respect the axis $\mu$, and $\ln \nu$ accounts for the molecular
symmetry. In the case of $C_{2v}$ molecules (like water) $\nu = 2$, due to the two possible degenerate angular orientations of the molecule [27].

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

The free energy at $(T_o, V_o)$ can be calculated as

$$F(T_o, V_o) = F_{lg}(T_o, V_o) - \int_{V_o}^{V_\infty} dV P_{ex}(T_o, V) + \frac{U(T_o, V_o)}{T_o},$$

(3)

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

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

(4)

giving

$$F(T_o, V_o) = F_{lg}(T_o, V_o) + \sum_{k=1}^{n} a_k(T_o) V_o^{-k} + \frac{U(T_o, V_o)}{T_o}. $$

(5)

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

$$F(T, V_o) = F(T_o, V_o) + 3R \ln(T/T_o) + \int_{T_o}^{T} \frac{dT}{T} \frac{\partial U(T, V_o)}{\partial T}. $$

(6)

The $3R \ln(T/T_o)$ term accounts for the ideal gas contribution to the free energy. Again, a fit of $U(T, V_o)$ vs $T$ is requested to evaluate the integral in the above expression. One possibility, which has been often found very successful for dense systems (small $V_o$) [26, 24], is to fit $U(T, V_o)$ vs $T$ according to the Tarazona law [28], i.e., $U(T, V_o) = b_0(V_o) + b_1(V_o) T^{3/5}$. Of course, for the present purposes, any functional form which correctly represents $U(T, V_o)$ can be selected.

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

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

This section describes how to calculate the average inherent structure energy $\langle e_{IS}(T, V) \rangle$. Recently, it has been shown that, on cooling at constant volume, on entering in 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 $1/T$ law [33, 19, 23, 21] for fragile liquids. Note that for silica, the prototype of a strong liquids, the $1/T$-law is not observed and $\langle e_{IS}(T, V) \rangle$ appears to approach a constant value on cooling [20].
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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 inherent structure, 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 by a sequence of minimization of the center 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 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 requested in the minimization procedure.

In Fig. 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 \( f_{\text{vib}}(e_{IS}, T, V) = U_{\text{vib}}(e_{IS}, T, V) - T S_{\text{vib}}(e_{IS}, T, V) \) is the free energy associated to the exploration of a basin of depth \( e_{IS} \) at temperature \( T \) and volume \( V \). \( f_{\text{vib}}(e_{IS}, T, V) \) takes into account both the kinetic energy of the system and the local structure of the basin with energy \( e_{IS} \). From a formal point of view, it is defined as

\[
 f_{\text{vib}}(e_{IS}, T, V) = -k_B T \ln \left( \sum' \int_{V_{\text{basin}}} \exp(-\beta [V(r^N) - e_{IS}]) d r^N \right),
\]

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

The evaluation of the integral requires the exact knowledge of the shape of the PES 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 \( f_{\text{vib}} \) is captured by the \( e_{IS} \) dependence of the density of states of the basin, evaluated at the IS configuration \([23],[24]\). In other words, the vibrational free energy is split into an 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 center of mass and the angles associated with the rotations around the three molecular principal inertia axis. Diagonalization is performed with standard numerical routines.

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

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

with

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

and

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

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

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

For the molecular systems studied so far, this unnecessary 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 $F_{\text{anh}}$ (and of course in $U_{\text{anh}}(T, V)$ and $S_{\text{anh}}(T, V)$). In other words, the anharmonicities are assumed to be identical in all basins. Under such approximation, $U_{\text{anh}}(T, V)$ can be calculated from the simulation data as

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

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

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

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

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

By incorporating the anharmonic corrections, which in models of simple fragile liquids studied so far are not particularly significant [22, 21], 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 [23, 20] and must be taken into account.

It is important to note that all the $e_{IS}$ dependence in the average basin free energy is carried by the term $V(V, e_{IS}) = \langle \sum_{i=1}^{6N-3} \ln \omega_i(e_{IS}) \rangle$. A parameterization of such quantity as a function of $e_{IS}$ allows to simply connect the basin free energy to
the basin depth. In all models studied so far [19, 21, 35, 31] a linear relation between basin depth and “basin shape” \( \mathcal{V} \), i.e.,

\[
\mathcal{V} = a(V) + b(V) e_{IS},
\]

correctly describes the simulation data (Fig. 3(a)).

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 to examine some of the proposed relation between dynamics and thermodynamics [36, 37, 16] connecting a purely dynamical quantity like the diffusion coefficient to a purely thermodynamical quantity \( S_{conf} \). The number of basins \( \Omega \) as a function of the basin depth \( e_{IS} \) has been recently evaluated for a few models [38, 22, 18, 23, 19, 20, 24, 21] and from the analysis of experimental data [39, 40, 41]. \( S_{conf}(T,V) \) — the logarithm of the number of explored basins — can be calculated as difference of the entropic part of Eq. (6) and Eq. (10), i.e., as

\[
S_{conf}(T,V) = S(T,V) - S_{vib}(T,V).
\]
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of depth $e_{IS}$. This information, together with the information of the $e_{IS}$ dependence of the basin shape (or volume) (Eq. (15)) completely defines the statistical properties of the landscape, at least in the range of $e_{IS}$ values sampled by the system in the studied $T$ region. The availability of $S_{conf}(e_{IS})$ (Fig. 3-(b)) and $\mathcal{V}(e_{IS})$ (Fig. 3-(a)) opens the possibility of a modellization 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 modellization 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 modellization, which appears to be consistent with the numerical evidence for fragile liquids, is based on the hypothesis that the number $\Omega(e_{IS}) \text{de}_{IS}$ of distinct basins of depth between $e_{IS}$ and $e_{IS} + \text{de}_{IS}$ in a system of $N$ atoms or molecules is described by a Gaussian distribution \[ 8, 25, 23, 19, 31 \], i.e.,

$$\Omega(e_{IS}) \text{de}_{IS} = e^{\alpha N} \frac{e^{- (e_{IS} - E_o)^2 / 2\sigma^2}}{(2\pi\sigma^2)^{1/2}} \text{de}_{IS}.$$ \hspace{1cm} (17)

Here the amplitude $e^{\alpha N}$ accounts for the total number of basins, $E_o$ has the role of energy scale and $\sigma^2$ measure the width of the distribution. One can understand the origin of such distribution invoking the central limit theorem. Indeed, in the absence of a diverging correlation length, in the thermodynamic limit, each IS can be decomposed in 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 Eq. (17).

Within the two assumptions of Eq. (17) — Gaussian distribution of basin depths — and Eq. (15) — linear dependence of the basin free energy on $e_{IS}$ — an exact evaluation of the partition function can be carried out. The corresponding Helmholtz free energy is given by \[ 15 \]

$$F(T, V) = -TS_{conf}(T, V) + \langle e_{IS}(T, V) \rangle + \mathcal{F}_{vib}(E', T) + k_B T b(V)(< e_{IS}(T, V) > - E').$$ \hspace{1cm} (18)

Here $E'$ is an arbitrarily fixed energy,

$$\langle e_{IS}(T) \rangle = (E_o(V) - b(V)\sigma^2(V)) - \beta\sigma^2(V),$$ \hspace{1cm} (19)

and

$$S_{conf}(T) / k_B = \alpha(V) N - (\langle e_{IS}(T, V) \rangle - E_o(V))^2 / 2\sigma^2(V).$$ \hspace{1cm} (20)

Note that, from a plot of $\langle e_{IS}(T) \rangle$ vs $1/T$, one can immediately evaluate two of the parameters of the gaussian distribution, $\sigma^2$ (from the slope) and $E_o$ (from the intercept). Similarly, from fitting $S_{conf}(T)$ according to Eq. (20), one can evaluate the last parameter $\alpha$ (see Fig. 3).

The fitting parameters $\alpha(V)$, $E_o(V)$, and $\sigma^2(V)$ depend in general on the volume. A study of the volume dependence of these parameters, associated to the $V$-dependence of the shape indicators ($a$ and $b$ in Eq. (15)) 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, — Eqs. (19) and (20) — 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 to an inherent structure. While in harmonic approximation such a quantity is unbounded, the real basin volume is not. Indeed, the sum of all basins volumes is equal to the volume of the system in configuration space. Anharmonic corrections, if properly handled, should compensate such overestimate, but at the present time, no model has been developed to correctly describe 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 shows already a clear two-step relaxation behavior in the dynamics. Indeed, the presence of a two-step relaxation is a signature that the system spends a time larger than the microscopic characteristic times around a well defined local minima.

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 to generalize the results and formulate a full thermodynamic description of the supercooled liquid state, only 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 [43, 31] for supercooled liquids only in terms of PEL properties. A better understanding of the nature of each contribution (configurational and vibrational) to quantities 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 visited in equilibrium, it is possible to write an out of equilibrium equation of state expressing $P$ as a function not only of $V$ and $T$ but also as a function of the (time dependent) depth of the explored basin.

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 the thermodynamics of supercooled liquids and glasses would improve significantly.

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