Thermodynamics of supercooled liquids in the inherent structure formalism: a case study

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Abstract. In this article we review the thermodynamics of liquids in the framework of the inherent structure formalism. We then present calculations of the distribution of the basins in the potential energy of a binary Lennard-Jones mixture as a function of temperature. The comparison between the numerical data and the theoretical formalism allows us to evaluate the degeneracy of the inherent structures in a bulk system and to estimate the energy of the lowest energy disordered state (the Kauzmann energy). We find that, around the mode-coupling temperature, the partition function of the liquid is approximated well by the product of two loosely coupled partition functions, one depending on the inherent structures quantities (depth of the basins and their degeneracy) and one describing the free energy of the liquid constrained in one typical basin.

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1. Introduction

The potential energy of a system composed by \(N\) interacting atoms is a complicated surface in a \(3N\)-dimension space. The motion of the system can be thought of as a trajectory over such a potential energy surface (PES). At different temperatures, the system explores different parts of the PES, according to the Boltzmann weight. The idea of focusing on the PES for understanding the physics of glass forming liquids can be traced back to the seminal (but talkative) paper of Goldstein \[1\]. He suggested that the dynamics of deeply supercooled liquids can be described in terms of a diffusive process of the system between different PES basins. At low temperatures the dynamics slows down since the liquid becomes trapped for a long time in a basin.

The concept of a basin in configuration space was formalized by Stillinger and Weber\[2\], who introduced a recipe, very well suited for numerical analysis, for
partitioning the PES into disjoint basins. The set of points in configuration space connected to the same local minimum via a steepest-descent trajectory defines uniquely the basin associated with this local minimum. Stillinger and Weber named the structure of the system in the minimum inherent-structure (IS) and the value of the PES at the minimum inherent-structure energy \( e_{IS} \).

The increased computational facilities have significantly improved the early efforts of studying the PES. Nowadays, an exhaustive search for all IS has been performed for clusters and complete maps of the inherent structure energies are available for several potential models [3]. For clusters, as well as for small proteins [4], the connectivity between all IS has also been evaluated, to provide a very informative map both of the thermodynamics [5] as well as of the dynamics in these small systems [6]. Small size systems, composed by 30 to 50 atoms with periodic boundary conditions, have also been studied in detail recently and almost exhaustive enumerations of all IS energies are now available [7, 8, 9].

In this article we review a theoretical framework in which the IS results can be interpreted in a convenient way (Sec. 2) and discuss the approximations requested for a factorization of the partition function in two functions, one describing the thermodynamics of the IS sub-system and one describing the thermodynamic of the exploration of one representative basin (Sec. 3). In the following two sections we present calculations of the temperature (Sec. 4) and IS energy (Sec. 5) dependence of the configurational entropy for a bulk system. Such calculations allow to quantify the properties of the PES for model systems and to probe the validity of the factorization approximation. New information on the equilibrium and aging dynamics of supercooled simple liquids is provided by the presented results. An account of the results has been reported in Ref. [10].

2. Theory

This section reviews the thermodynamic formulation proposed by Stillinger and Weber [2], focusing on the concept of basins in configuration space.

The partition function of a system composed by \( N \) identical atoms of mass \( m \), after the integration over the momentum variables is

\[
Z_N = \lambda^{-3N} \int \exp(-\beta V(r^N)) dr^N
\]

where \( \lambda = h\sqrt{\beta/2\pi m} \). The integral over the configuration space \( r^N \) can be separated into a sum over all distinct basins

\[
Z_N = \lambda^{-3N} \sum_{\alpha} \exp(-\beta \Phi_{\alpha}) \int_{R_{\alpha}} \exp(-\beta \Delta_{\alpha}(r^N)) dr^N
\]

where \( R_{\alpha} \) is the set of points composing the basin \( \alpha \), \( \Phi_{\alpha} \) is the potential energy of the minimum \( \alpha \) and the non-negative quantity \( \Delta_{\alpha}(r^N) \) measures the potential energy at a point \( r^N \) belonging to the basin \( \alpha \) relative to the minimum. By classifying the minima
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According to their IS energy $e_{IS}$, the sum over the basins can be separated in a sum over all possible values of $e_{IS}$ and a sum over all basins $\alpha'$ with the same $e_{IS}$ value.

$$Z_N = \lambda^{-3N} \sum_{e_{IS}} \exp(-\beta e_{IS}) \sum_{\alpha'} \int_{R_{\alpha'}} \exp(-\beta \Delta\alpha'(r^N)) \, dr^N$$ (3)

Following Stillinger and Weber, we introduce an IS density of states $\Omega(e_{IS})$, which counts the number of distinct basins with IS energy between $e_{IS}$ and $e_{IS} + \delta e_{IS}$ and define a basin free energy $f(\beta, e_{IS})$ as the average $e_{IS}$ basin free energy, according to

$$-\beta f(\beta, e_{IS}) \equiv \ln \left( \frac{\lambda^{-3N} \sum_{\alpha'} \int_{R_{\alpha'}} \exp(-\beta \Delta\alpha'(r^N)) \, dr^N}{\delta e_{IS} \Omega(e_{IS})} \right)$$ (4)

If all basins with the same $e_{IS}$ energy have the same statistical properties then $f(\beta, e_{IS})$ coincides with the free energy of a system constrained to sample only one basin and which does not know of the existence of the other equivalent $\delta e_{IS} \Omega(e_{IS})$ basins. $Z_N$ can be expressed in terms of PES quantities, as

$$Z_N = \int d e_{IS} \Omega(e_{IS}) \exp(-\beta e_{IS} - \beta f(\beta, e_{IS}))$$ (5)

Performing a maximum integral evaluation of the partition function, the free energy $F$ of the system can be expressed in the thermodynamic limit as

$$F = e^*_T - T S_{conf}(e^*_T) + f(\beta, e^*_T)$$ (6)

where $e^*(T)$ is the $e_{IS}$ value which maximizes the integrand and $S_{conf}(e_{IS}) = k_B \ln(\delta e_{IS} \Omega(e_{IS}))$. If we separate now $f(\beta, e)$ in its energetic $u_b$ and entropic $s_b$ contribution, we immediately notice that the entropy associated with the basin degeneracy, $S_{conf}(T)$, can be calculated as the difference between the system entropy and $s_b$, the entropy of the system constrained in an IS $e^*$. In the present formalism, if one excludes from the sum in the partition function the crystalline IS, then one can identify $F$ as the fluid free energy for all $T$.

The choice of separating the liquid free energy in a sum of two inter-related contributions (via the $e_{IS}$ dependence of $f$) has been often used in the past, for example in estimating the configurational entropy from available experimental data[11]. In this case, the basin entropy is identified with the entropy of the stable crystal at the same thermodynamics point. Such an identification is based on the idea that the vibrational properties of a system constrained in a deep basin are similar to the properties of the close crystalline structure. More recently, the consequences of such separation for several thermodynamic quantities have been explicitly worked out[12]. For recent related work see also [13, 14]

3. Low $T$ approximation

There are two interesting cases which may help understanding the low $T$ dynamics of liquids. These cases are connected to specific forms of $f(\beta, e_{IS})$. The first describes the case where $f(\beta, e_{IS}) \approx f(\beta)$, i.e. there is no $T$-dependence through $e_{IS}$. In this case
basins are characterized by approximately the same shape in configuration space, an hypothesis which can be tested by studying the $e_{IS}$ dependence of the density of states. In this approximation Eq. (5) factorizes in

$$Z_N \approx Z^{IS} \cdot Z^b$$

where

$$Z^{IS} = \int \Omega(e_{IS}) \exp(-\beta e_{IS}) \, de_{IS}$$

and

$$Z^b = \exp(-\beta f(\beta))$$

In the range of $T$ where this approximation holds, the system can be tough of as two weakly coupled subsystem: the $IS$-subsystem, which has now been transformed in a system with levels labeled by the $e_{IS}$ value with degeneracy $\Omega(e_{IS})$, and the basin subsystem which describe the motion in the characteristic basin. The coupling between the two subsystem, which of course allows for the equilibration process between the two subsystems, is due to the weak $T$ dependence of $e_{IS}$, which is neglected in the present approximation.

The second case is the case when $\beta f(\beta, e_{IS}) \approx g(\beta) + h(e_{IS})$, i.e. when the $T$ and $e_{IS}$ dependence are not mixed. This case is realized for example in the case where at different $T$ the system populate basins which are always harmonic, but different in their density of states\[14\]. In this second case, a factorization of $Z_N$ as in Eq. (7) is also possible by redefining the density of states to include the basin volume in configuration space, as $\Omega(e_{IS})e^{h(e_{IS})}$\[14\].

Analysis of computer simulation data allows to look for the existence of a $T$ range where the factorization approximation holds. Indeed, the probability density of extracting from a system in thermal equilibrium at temperature $T$ a configuration belonging to a basin with IS energy $e_{IS}$ is

$$P(e_{IS}, T) = \frac{\Omega(e_{IS}) \exp(-\beta e_{IS} - \beta f(\beta, e_{IS}))}{Z_N(T)}$$

If the factorization approximation holds, then the only $e_{IS}$ dependence in the rhs of

$$\ln[P(e_{IS}, T)e_{IS}] + \beta e_{IS} = S_{conf}(e_{IS})/k_B - \ln[Z_N(\beta)] - \beta f(\beta, e_{IS})$$

is contained in $S_{conf}$. This imply that curves for different $T$ can be superimposed after a shift of a $T$-dependent quantity. The resulting $e_{IS}$ master curve is, except for an unknown constant, the $e_{IS}$ configurational entropy.

4. System

We have studied the well-known 80-20 Lennard-Jones $A - B$ binary mixture (BMLJ), composed by 1000 atoms in a volume $V_o = (9.4)^3$, corresponding to a reduced density of 1.2039. Units of length, energy and are defined by the $\sigma$ and $\epsilon$ of the $A - A$ Lennard
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Jones interaction potential, and the unit of mass by the mass of atom A. The pair potential is defined in Ref. [15]. The equilibrium and out-of-equilibrium slow dynamics has been studied extensively. The critical temperature of Mode Coupling Theory for this system is 0.435 [15].

New simulations, covering the range 0.446 \( \leq T \leq 5.0 \), have been performed in the canonical ensemble by coupling the system to a Nose’-Hoover thermostat [16]. From simulations lasting more than 60M steps, we have extracted 1000 equally spaced configurations and we have calculated for each of them the corresponding IS.

5. Temperature Dependence of the configurational entropy

We have estimated the \( T \)-dependence configurational entropy for the BMLJ as difference of the liquid entropy and of the basin entropy, as discussed in section 2. An independent (and consistent) estimate of the same quantity in the same system has been performed with a similar procedure by Coluzzi et al. [17, 18]. For related work see also Refs. [19].

The entropy of the liquid has been calculated via thermodynamic integration starting from the ideal gas binary mixture reference point, along the \( T = 5.0 \) isotherm, up to the studied \( \rho = 1.2 \) density. In the following we call \( C \) the state point \( T = 5.0, \rho = 1.2 \). The entropy of the liquid in \( C \) can be written as

\[
S(C) = S_{\text{ideal-gas}}(C) + \frac{U(C)}{T} + \int_{\infty}^{V_0} \frac{P_{\text{ex}} dV}{T}
\]

where

\[
S_{\text{ideal-gas}}(T, \rho) = -\frac{N_A}{N} \ln\left(\frac{N_A}{N}\right) - \frac{N_B}{N} \ln\left(\frac{N_B}{N}\right) + \frac{3}{2} \frac{\ln\left(\frac{cmV_0^2}{\hbar^22\pi}\right)}{\beta h^2} - \ln\left(\frac{N_e}{e}\right)
\]

\( P_{\text{ex}} \) is the excess pressure over the ideal gas value, \( U \) is the potential energy, and \( e \) is the energy per particle. Fig. [4] shows the excess pressure as a function of the volume calculated from twenty-six independent molecular dynamics simulations. At large volumes, the calculated excess pressure coincides with the first correction to the ideal gas law which can be analytically calculated from the first virial coefficient of the binary mixture, \( B_2(T) \), which in the case of our system is equal to \( B_2(T = 5.0) = 0.53622 \). To decrease the numerical integration error we analytically calculate the contribution to the integral arising from the first virial corrections and integrate over the volume only \( P_{\text{ex}} - B_2(T)k_B T(N/V)^2 \). As a result, we obtain \( S(C)/k_B = 8061.7 \)[20].

The entropy at any \( T \) along the studied isochoric path can then be calculated as

\[
S(T, \rho = 1.2) = S(C) + \int_{T=5.0}^{T'} \frac{C_V(T')}{T'} \,dT'
\]

where \( C_V(T) = dU(T)/dT + 3/2Nk_B \) is calculated from the \( T \)-dependence of the system average potential energy \( U \) obtained from the simulations. We find that, in agreement with recent theoretical predictions[21], the \( T \) dependence of \( U \) along the studied isochore is very well described by the law \( U(T) \sim T^{3/5} \) (See Fig. [4]), which produces a contribution to the liquid entropy varying as \( T^{-2/5} \). The use of the \( T^{-2/5} \) law provides a reliable extrapolation of \( S_{\text{liquid}} \) below the lowest studied \( T \).
Figure 1. Excess pressure as a function of the volume at $T = 5.0$. The dashed line is the analytically calculated first virial correction to the pressure.

Figure 2. Potential energy as a function of $T^{3/5}$ for the BMLJ system. The inset show the same data in liner scale. The continuous line is the fit to $U = a + bT^{3/5}$.

To estimate the basin entropy, we assume that at the lowest studied $T$, the unknown $f(\beta, e)$ can be approximated by the harmonic free energy of a disordered system characterized by the eigenfrequencies spectrum calculated from the IS at the corresponding $T$. In this approximation, the difference between the entropy of the liquid and the entropy of the harmonic disordered solid coincides with the configurational entropy. We evaluate the entropy of the disordered solid in the harmonic approximation as

$$S_{\text{disordered-solid}}(T, V) = \sum_{j=1}^{3N-3} 1 - \ln(\beta \hbar \omega_j)$$

where $\omega_j$ is the frequency of the $j$-th normal mode. The $e_{\text{IS}}$-dependence in
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\(S_{\text{disordered-solid}}(T, V)\) enters via the \(e_{IS}\)-dependence of the density of states. Consistently with the estimate of the \(e_{IS}\) dependence of \(f(e_{IS}, T)\) discussed below, we find (see Fig. 3-left) that the \(T\) dependence of the density of states accounts for only a few percent of the \(T\)-change in \(S_{\text{disordered-solid}}\) at low \(T\).

The \(T\) dependence of the evaluated liquid and disordered solid entropies is reported in Fig.3-left. The \(T\) dependence of the configurational entropy (difference between \(S_{\text{liquid}}\) and \(S_{\text{disordered-solid}}\)) is reported in Fig.3-middle. We note that, if the extrapolations are reliable, the configurational entropy vanishes at \(T = 0.297 \pm 0.01\), which defines the Kauzmann temperature \(T_K\) for the studied binary mixture, in agreement with the findings of Coluzzi et al.\[17, 18\]. Note that the configuration entropy around \(T_{MCT} = 0.435\) is halfway between \(T_K\) and the high \(T\) value, suggesting that the ordering process in configuration space at the lowest temperature which we have been able to equilibrate is far from being complete. Of course, the present data do not furnish a full proof of the existence of a finite \(T\) at which \(S_{\text{conf}}\) goes to zero, being based on a large (but apparently reliable, see Fig.2) extrapolation in \(T\). We also note that the ratio between \(T_K\) and \(T_{MCT}\) support the view that the studied system has intermediate fragility character, as recently predicted by Angell and coworkers on the basis of a comparison between experimental results and numerical data for the same system.\[23\].

6. IS-energy dependence of the configurational entropy

In this section we show that in the BMLJ case, for \(T < 0.8\), the factorization approximation discussed in Sec. 3 is indeed satisfied. The possibility of separating the IS subsystem thermodynamics from the basin thermodynamics allow us to calculate the \(e_{IS}\) dependence of the configurational entropy and thus to estimate the number of basins in configuration space with the same \(e_{IS}\) energy.

To test the validity of the factorization approximation, we evaluate the lhs of Eq. 11, i.e. we calculate the \(e_{IS}\) dependence of \(\ln(P(e_{IS}, T)) + e_{IS}/T\). As discussed in Sec. 3, if \(f(\beta, e_{IS})\) has only a weak dependence on \(e_{IS}\), then it must be possible to superimpose curves at different temperatures which overlap in \(e_{IS}\). Then, the resulting \(e_{IS}\)-dependent curve is, except for an unknown constant, \(S_{\text{conf}}(e_{IS})\), in the \(e_{IS}\) range accessed at the studied \(T\).

This procedure is displayed in Fig.4. We note that while below \(T = 0.8\) curves for different \(T\) lie on the same master curve, above \(T = 0.8\), curves for different \(T\) have different \(e_{IS}\) dependence, highlighting the progressive \(e_{IS}\)-dependence of \(f(\beta, e_{IS})\).

The data presented in Fig. 4 are particularly relevant. They show that, below \(T = 0.8\), the IS can be treated as a system of levels characterized by an energy value \(e_{IS}\) and an associated degeneracy \(\Omega(e_{IS})\). Thus, for the \(e_{IS}\) subsystem it is possible to use the standard thermodynamics relations to evaluate the \(T\)-dependence of the average energy and entropy. In this respect, the \(T\) dependent configurational entropy (but only
Figure 3. Left: Liquid (circles) and disordered-solid (squares) entropies as a function of \( T \). The diamonds show the \( T \) dependence of the disordered solid entropy, once the explicit \( T \) dependence is subtracted, to highlight the weak residual \( T \) dependence due to the \( T \)-dependence of the density of states. Such weak residual \( T \)-dependence has been extrapolated to lower \( T \) via a quadratic fit and used to provide an analytic expression for the \( T \) dependence of the disordered solid entropy. Middle: \( T \)-dependence of the configurational entropy. Right: \( T \)-dependence of the IS energy for the BMLJ system as determined from the simulation (circles) and from Eq. (16) (solid line).

below \( T = 0.8 \)) can be evaluated as

\[
\frac{dS_{\text{conf}}(T)}{de_{\text{IS}}(T)} = \frac{1}{T} \quad e_{\text{IS}}(T) = e_{\text{IS}}(T_K) + \int_{T_k}^{T} T dS_{\text{conf}}(T) \tag{16}
\]

By integrating the configurational entropy from \( T_K \) upward, it is possible to calculate the \( T \) dependence of \( e_{\text{IS}} \). The unknown integration constant \( e_{\text{IS}}(T_K) \) can be calculated by comparing the obtained expression with the \( e_{\text{IS}}(T) \)-dependence calculated directly from the simulation in the region \( T \leq 0.8 \) (see also Ref. [24]). The present analysis (see Fig. 3-right) predicts \( e_{\text{IS}}(T_K) = -7.82 \pm 0.01 \).

From \( S(T) \), evaluated in the previous Section, and from \( e_{\text{IS}}(T) \), evaluated according to Eq. (16), it is possible to eliminate the \( T \) dependence and to calculate the \( e_{\text{IS}} \) dependence of the configurational entropy in an absolute scale, which can be compared with the one calculated independently — but with an unknown constant — via the superposition of the different \( \ln(P(e_{\text{IS}}, T)) + e_{\text{IS}}/T \) curves. Such a comparison is done in Fig. 4. The agreement between the two set of measurements confirms the validity of the analysis presented in this article and the quality of the factorization approximation.
Figure 4. Top: Distributions $P(e_{IS}, T)$ of the $IS$ energy (per atom) for different equilibrium temperatures $T$. From left to right: $T = 0.446, 0.466, 0.5, 0.55, 0.6, 0.8, 1.0, 2.0, 4.0$. Middle: $\ln[P(e_{IS}, T)] + \beta e_{IS}$, for six different equilibrium temperatures $T$. Same symbols as in the top panel. Bottom: Data in the middle panel (plus data corresponding to other $T$) are displayed shifted to maximize the overlap between curves with different $T$ and the overlap with $S_{conf}(e_{IS})$ (in absolute units), calculated as discussed in the text and shown here as full line. The curves which do not lay on the continuous line correspond to $T = 5.0, 4.0, 2.0, 1.5, 1.0, 0.8$, from bottom to top.

Before concluding this section, we note that an estimate of the $e_{IS}$ dependence of the configurational entropy, based on the analysis of experimental data have been presented in Ref. [25]. Analysis of the configurational entropy as a function of internal system parameter’s (which conceptually are equivalent to the $e_{IS}$ choice adopted in the present work) have been reported in Ref. [26, 27].
7. Conclusions

The data and the analysis reported in this article offer a detailed thermodynamic description of the supercooled state, based on the formalism proposed by Stillinger and Weber. In particular we have presented a quantitative evaluation of the degeneracy of the inherent structures (which before was only calculated for systems composed by less than 50 atoms[7, 8]) for a bulk system. We consider particularly relevant the presented evidence that in the supercooled states (below $T = 0.8$ for the studied system) the thermodynamics of the inherent structures almost completely decouples from the “vibrational” thermodynamics (i.e. from the process of exploration of the IS basin). It is particularly important to notice that a thermodynamics approach for the inherent structures subsystem becomes possible in supercooled states. The description of supercooled liquids as composed by two weakly coupled subsystems — the IS subsystem and the “vibrational” basin subsystem — offers stimulating ideas both for a microscopic understanding of the out-of-equilibrium thermodynamics recently proposed[28] (since if the factorization were exact, one could think of keeping the two subsystem coupled to two different temperatures) and the aging processes[29], as well as for the still missing theoretical quantitative description of the slow dynamics below the MCT temperature. A first step in the direction of estimating the temperature at which the configurational subsystem is in quasi-equilibrium during an aging process has been recently reported[30, 31].

Finally, we stress that the description we have presented refers to a constant volume system. In this respect, it is based on one internal parameter only (in the language of Davies and Jones[32]), which we have identified with $e_{IS}$. In a full treatment, at least one other internal parameter would be necessary, to discriminate between basins with the same $e_{IS}$ but different volume. We plan to further test the validity of such one-internal parameter description for isochoric cooling.

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