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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 (which we define as 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-structure quantities (depths of the basins and their degeneracy) and one describing the free energy of the liquid constrained in one typical basin.

1. Introduction

The potential energy of a system composed of N interacting atoms is a complicated surface in a $3N$ -dimensional 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 discursive) paper of Goldstein [1]. He suggested that the dynamics of deeply supercooled liquids can be described in terms of a process of diffusion 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 the inherent structure (IS) and the value of the PES at the minimum the inherent-structure energy (e_{IS}).

Enhanced computational facilities have led to significant improvements on the early efforts at 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] and of the dynamics in these small systems [6]. Small-size systems, composed of 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 [7–9].

In this article we review a theoretical framework in which the IS results can be interpreted in a convenient way (section 2) and discuss the approximations required for a factorization of the partition function into two functions, one describing the thermodynamics of the IS subsystem and one describing the thermodynamics of the exploration of one representative basin (section 3). In the following two sections we present calculations of the temperature (section 5) and IS energy (section 6) dependence of the configurational entropy for a bulk system. Such calculations allow one 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 results presented. An account of the results has been reported in reference [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

$$Z_N = \lambda^{-3N} \int \exp(-\beta V(\mathbf{r}^N)) d\mathbf{r}^N \quad (1)$$

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

$$Z_N = \lambda^{-3N} \sum_{\alpha} \exp(-\beta \Phi_{\alpha}) \int_{R_{\alpha}} \exp(-\beta \Delta_{\alpha}(\mathbf{r}^N)) d\mathbf{r}^N \quad (2)$$

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

$$Z_N = \lambda^{-3N} \sum_{e_{IS}} \exp(-\beta e_{IS}) \sum_{\alpha'} \int_{R_{\alpha'}} \exp(-\beta \Delta_{\alpha'}(\mathbf{r}^N)) d\mathbf{r}^N. \quad (3)$$

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 basin free energy—where the averaging is performed over all basins with IS energy e_{IS} —according to

$$-\beta f(\beta, e_{IS}) \equiv \ln \left(\left[\lambda^{-3N} \sum_{\alpha'} \int_{R_{\alpha'}} \exp(-\beta \Delta_{\alpha'}(\mathbf{r}^N)) d\mathbf{r}^N \right] / [\delta e_{IS} \Omega(e_{IS})] \right). \quad (4)$$

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 is unaffected by the existence of the other equivalent $\delta e_{IS} \Omega(e_{IS})$ basins. Z_N can be expressed in terms of PES quantities, as

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

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

$$F = e_{IS}^* - T S_{conf}(e_{IS}^*) + f(\beta, e_{IS}^*) \quad (6)$$

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 now separate $f(\beta, e)$ into its energetic (u_b) and entropic (s_b) contributions, 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* to be in an IS with energy 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 into a sum of two interrelated contributions (via the e_{IS} -dependence of f) has often been 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 thermodynamic point. Such an identification is based on the idea that the vibrational properties of a system constrained to be in a deep basin are similar to the properties of the close crystalline structure. More recently, the consequences of such a 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 in 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, a hypothesis which can be tested by studying the e_{IS} -dependence of the density of states. In this approximation equation (5) factories as

$$Z_N \approx Z^{IS} Z^b \quad (7)$$

where

$$Z^{IS} = \int \Omega(e_{IS}) \exp(-\beta e_{IS}) de_{IS} \quad (8)$$

and

$$Z^b = \exp(-\beta f(\beta)). \quad (9)$$

In the range of T where this approximation holds, the system can be thought of as two weakly coupled subsystems: the IS subsystem, which has now been transformed into a system with levels labelled by the e_{IS} -value with degeneracy $\Omega(e_{IS})$, and the basin subsystem which describes the motion in the characteristic basin. The coupling between the two subsystems, which of course allows for the process of equilibration 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 that where $\beta f(\beta, e_{IS}) \approx g(\beta) + h(e_{IS})$, i.e. where the T - and e_{IS} -dependences are not mixed. This case is realized for example in the case where at different T the system populates basins which are always *harmonic*, but differ in their densities of states [14]. In this second case, a factorization of Z_N as in equation (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 us to look for the existence of a T -range where the factorization approximation holds. Indeed, the probability density for extracting from a system in thermal equilibrium at temperature T a configuration belonging to a basin with IS energy e_{IS} is

$$P(e_{IS}, T) = \frac{\Omega(e_{IS}) \exp(-\beta e_{IS} - \beta f(\beta, e_{IS}))}{Z_N(T)}. \quad (10)$$

If the factorization approximation holds (i.e. for either case), then the only e_{IS} -dependence in the right-hand side of

$$\ln[P(e_{IS}, T) \delta e_{IS}] + \beta e_{IS} = S_{conf}(e_{IS})/k_B - \ln[Z_N(\beta)] - \beta f(\beta, e_{IS}) \quad (11)$$

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

4. The system

We have studied the well-known 80–20 Lennard-Jones A–B binary mixture (BMLJ), composed of 1000 atoms in a volume $V_0 = (9.4)^3$, corresponding to a reduced density of 1.2039. The units of length and energy are defined to be σ and ϵ for the A–A Lennard-Jones interaction potential, and the unit of mass is taken as the mass of atom A. The pair potential is defined in reference [15]. The equilibrium and out-of-equilibrium slow dynamics have 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 Nosé–Hoover thermostat [16]. From simulations over more than 60×10^6 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 of the configurational entropy for the BMLJ as the difference of the liquid entropy and the basin entropy, as discussed in section 2. An independent (and consistent) estimate of the same quantity in the same system has been previously obtained by a similar procedure by Coluzzi *et al* [17, 18]. For related work see also references [19].

The entropy of the liquid has been calculated via thermodynamic integration starting from the ideal-gas binary-mixture reference point ($T = 5.0$, $\rho \rightarrow 0$) along the isotherm $T = 5.0$, up to the density studied, $\rho = 1.2$. In the following we call ($T = 5.0$, $\rho = 1.2$) the state point C. The entropy of the liquid at C can be written as

$$S(C) = S_{ideal\ gas}(C) + \frac{U(C)}{T} + \int_{\infty}^{V_0} \frac{P_{ex} dV}{T} \quad (12)$$

where

$$\frac{S_{ideal\ gas}(T, \rho)}{Nk_B} = -\frac{N_A}{N} \ln\left(\frac{N_A}{N}\right) - \frac{N_B}{N} \ln\left(\frac{N_B}{N}\right) + \frac{3}{2} \ln\left(\frac{emV^{2/3}}{\beta\hbar^2 2\pi}\right) - \ln\left(\frac{N}{e}\right) \quad (13)$$

also takes into account the entropy of mixing. P_{ex} is the excess pressure over the ideal-gas value, U is the potential energy and e is the Neper number. Figure 1 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

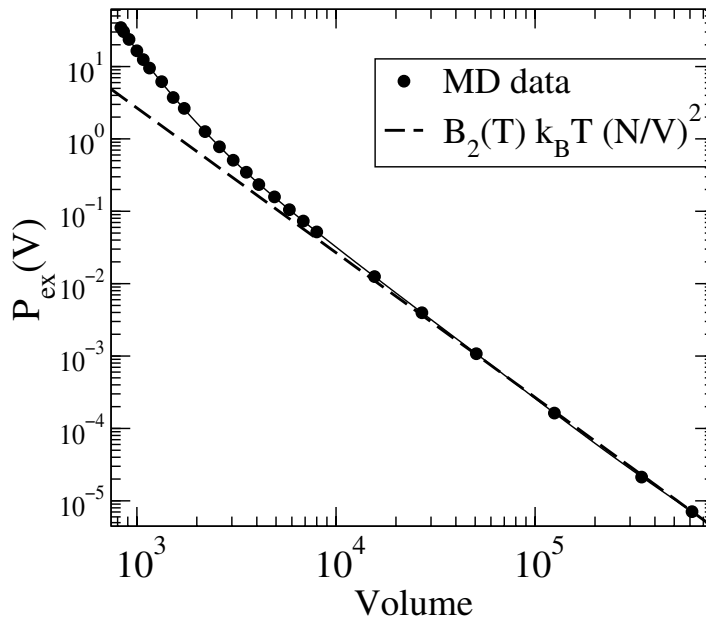


Figure 1. Excess pressure as a function of the volume at $T = 5.0$. The dashed line is the analytically calculated first virial correction to the pressure.

coefficient of the binary mixture, $B_2(T)$ [20], 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: $P_{ex} - B_2(T)k_B T(N/V)^2$. As a result, we obtain $S(C)/k_B = 8061.7^\dagger$.

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

$$S(T, \rho = 1.2) = S(C) + \int_{T=5.0}^T \frac{C_V(T')}{T'} dT' \quad (14)$$

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 isochore studied is very well described by the law $U(T) \sim T^{3/5}$ (see figure 2), 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_{liquid} below the lowest T studied.

To estimate the basin entropy, we assume that at the lowest T studied, 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

$$S_{\text{disordered solid}}(T, V) = \sum_{j=1}^{3N-3} 1 - \ln(\beta \hbar \omega_j) \quad (15)$$

† In equation (12) we have used $\hbar = 0.063507 \text{ kJ mol}^{-1} \text{ ps}^{-1}$. We have assumed the A–A LJ interaction potential to be equal to 1 kJ mol^{-1} , the unit of length to be equal to 1 nm , the unit of time to be 1 ps . With this choice, the three terms in equation (12) contribute 10734.1 , $1678.5/5$, 2336.7 respectively.

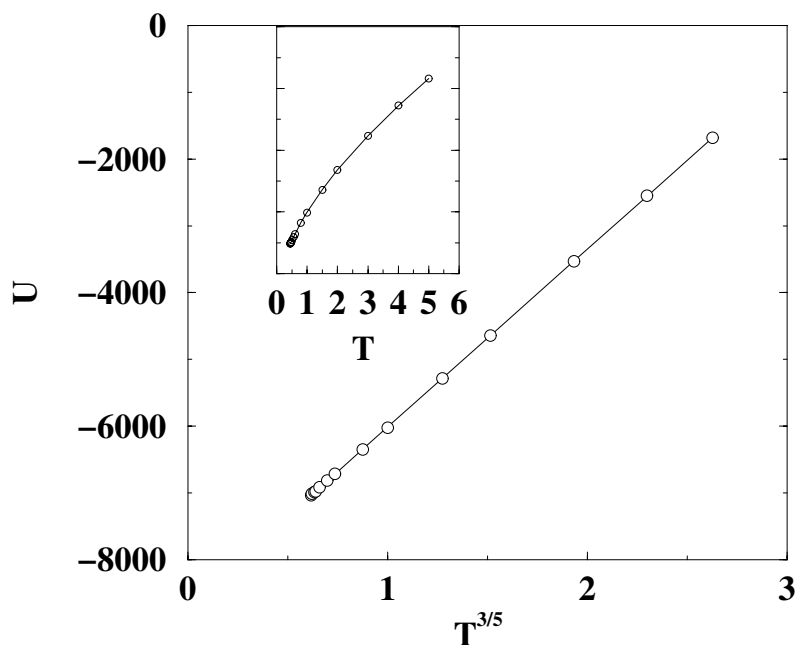


Figure 2. Potential energy as a function of $T^{3/5}$ for the BMLJ system. The inset shows the same data on a linear scale. The continuous line is a fit to $U = a + bT^{3/5}$.

where ω_j is the frequency of the j th normal mode. For the binary-mixture Lennard-Jones case under study, the vibrational energy (defined as the potential energy minus e_{IS}) is equal to $3Nk_B T/2$ over a large T -range, supporting the harmonic approximation employed. Further work is required to assess the validity of the harmonic approximation, especially since it has been suggested that even low- T basins may retain some ruggedness (see for example Sastry *et al* in reference [22]).

The e_{IS} -dependence in $S_{\text{disordered solid}}(T, V)$ 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 figure 3, left) that the T -dependence of the density of states accounts for only a few per cent of the T -change in $S_{\text{disordered solid}}$ at low T .

The T -dependence of the liquid and disordered solid entropies evaluated is reported in figure 3, left. The T -dependence of the configurational entropy (the difference between S_{liquid} and $S_{\text{disordered solid}}$) is reported in figure 3, middle. We note that, if the extrapolations are reliable, the configurational entropy vanishes at $T = 0.297 \pm 0.01$, which we define as T_K in analogy with the Kauzmann temperature [23], since at T_K the liquid configuration entropy becomes equal to the crystal configuration entropy. The calculated T_K -value agrees with the previous findings of Coluzzi *et al* [17, 18]. Note that the Kauzmann temperature is defined by Kauzmann as the temperature at which the liquid entropy becomes equal to the crystal entropy. Kauzmann's definition coincides with the definition used here only if the crystal vibrational entropy is a good approximation to the basin vibrational entropy. The approximation of S_{vib} via the entropy of the crystalline form is not required in the IS formalism, where—in principle— S_{vib} is calculated from the shape of the very basin in which the system is trapped. Note also 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 at which we have been able to equilibrate is far from being complete. Of course, the present data do

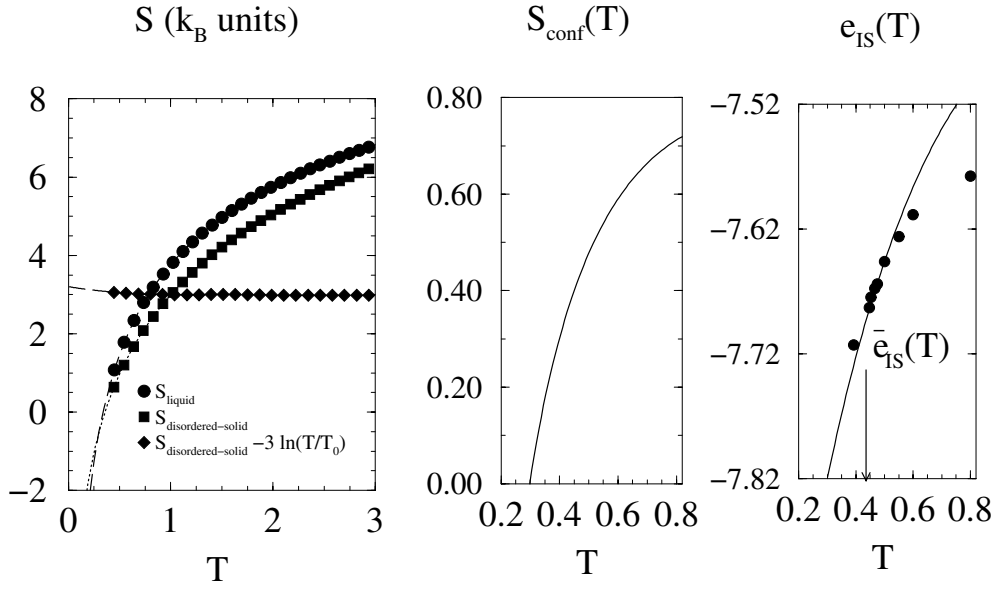


Figure 3. Left: liquid (circles) and disordered solid (squares) entropies as functions of T . The diamonds show the T -dependence of the disordered solid entropy, once the explicit T -dependence is subtracted, to highlight the weak residual T -dependence due to the T -dependence of the density of states. 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: the T -dependence of the configurational entropy. Right: the T -dependence of the IS energy for the BMLJ system as determined from the simulation (circles) and from equation (16) (solid line).

not furnish a full proof of the existence of a finite T at which S_{conf} goes to zero, being based on a large (but apparently reliable; see figure 2) extrapolation in T . The ratio between T_K and T_{MCT} supports the view that the system studied has intermediate fragility character, as recently predicted by Angell and co-workers on the basis of a comparison between experimental results and numerical data for the same system [24].

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 section 3 is indeed satisfied. The possibility of separating the IS subsystem thermodynamics from the basin thermodynamics allows 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 left-hand side of equation (11), i.e. we calculate the e_{IS} -dependence of $\ln(P(e_{IS}, T)) + e_{IS}/T$. As discussed in section 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 temperature studied.

This procedure is displayed in figure 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

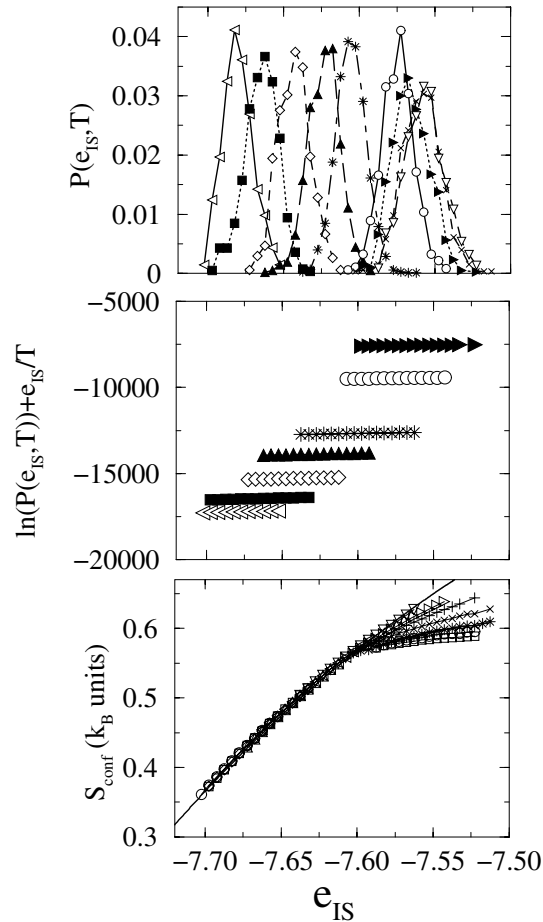


Figure 4. Top: distributions $P(e_{IS}, T)$ of the IS energy (per atom) for different equilibrium temperatures T . From left to right: $T = 0.446, 0.466, 0.5, 0.55, 0.6, 0.8, 1.0, 2.0, 4.0$. Middle: $\ln[P(e_{IS}, T)] + \beta e_{IS}$, for six different equilibrium temperatures T (same symbols as in the top panel). Bottom: data in the middle panel (plus data corresponding to other values of T and the overlap with $S_{conf}(e_{IS})$ (in absolute units), calculated as discussed in the text and shown here as a full line. The curves which do not lie on the continuous line correspond to $T = 5.0, 4.0, 2.0, 1.5, 1.0, 0.8$, from bottom to top.

e_{IS} -dependences, indicating the progressive e_{IS} -dependence of $f(\beta, e_{IS})$.

The data presented in figure 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 thermodynamic relations to evaluate the T -dependence of the average energy and entropy. In this respect, the T -dependent configurational entropy (but only below $T = 0.8$) can be evaluated as

$$\frac{dS_{conf}(T)}{de_{IS}(T)} = \frac{1}{T} \quad e_{IS}(T) = e_{IS}(T_K) + \int_{T_K}^T T dS_{conf}(T) \quad (16)$$

where $e_{IS}(T_K)$, which we define as the Kauzmann energy, is the IS energy of the lowest disordered configuration. Of course, the number of basins of energy $e_{IS}(T_K)$ is non-extensive,

since the corresponding configurational entropy is zero. By integrating the configurational entropy from T_K upward, it is possible to calculate the T -dependence of e_{IS} . The unknown integration constant $e_{IS}(T_K)$ can be calculated by comparing the expression obtained with the $e_{IS}(T)$ dependence calculated directly from the simulation in the region $T \leq 0.8$ (see also reference [22]). The present analysis (see figure 3, right) predicts $e_{IS}(T_K) = -7.82 \pm 0.01$.

From $S(T)$, evaluated in the previous section, and from $e_{IS}(T)$, evaluated according to equation (16), it is possible to eliminate the T -dependence and to calculate the e_{IS} -dependence of the configurational entropy on an absolute scale, which can be compared with the one calculated independently—but with an unknown constant—via the superposition of the different $\ln(P(e_{IS}, T)) + e_{IS}/T$ curves. Such a comparison is shown in figure 4. The agreement between the two sets of measurements confirms the validity of the analysis presented in this article and the quality of the factorization approximation.

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, has been presented in reference [25]. Analyses of the configurational entropy as a function of internal system parameters (which conceptually are equivalent to the choice of e_{IS} adopted in the present work) have been reported in references [26, 27].

7. Conclusions

The data and the analysis reported in this article offer a detailed thermodynamic description of the supercooling 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 had previously only been calculated for systems composed of less than 50 atoms [7, 8]) for a bulk system. We consider particularly relevant the evidence presented that in supercooled states (below $T = 0.8$ for the system studied) 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 to the inherent-structure subsystem becomes possible for supercooled states. The description of supercooled liquids as composed of two weakly coupled subsystems—the IS subsystem and the ‘vibrational’ basin subsystem—generates stimulating ideas both as regards a microscopic understanding of the out-of-equilibrium thermodynamics proposed recently [28] (since if the factorization were exact, one could think of keeping the two subsystems coupled to two different temperatures) and as regards the aging processes [29], as well as the still lacking 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 reported recently [30, 31].

Finally, we stress that the description that 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 value of e_{IS} but different volumes. We plan to further test the validity of such one-internal-parameter description for isochoric cooling.

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