Inherent Structure Entropy of Supercooled Liquids

F. Sciortino,1 W. Kob,2 and P. Tartaglia1

1Dipartimento di Fisica and Istituto Nazionale per la Fisica della Materia, Università di Roma La Sapienza, Piazzale Aldo Moro 2, I-00185, Roma, Italy
2Institut für Physik, Johannes Gutenberg-Universität, Staudinger Weg 7, D-55099 Mainz, Germany

(Received 7 June 1999)

We present a quantitative description of the thermodynamics in a supercooled binary Lennard-Jones liquid via the evaluation of the degeneracy of the inherent structures, i.e., of the number of potential energy basins in configuration space. We find that the contribution of the inherent structures to the free energy of the liquid almost completely decouples from the vibrational contribution. An important by-product of the presented analysis is the determination of the Kauzmann temperature for the studied system.

PACS numbers: 61.20.Ja, 64.70.Ja

In recent years, a significant effort has been devoted to understand the fundamental nature of glass-forming materials, a long-standing open problem in condensed matter physics [1]. Theoretical [2–4], experimental [5], and numerical efforts [6] have broadened our knowledge of the physical mechanisms responsible for the dramatic slowing down of the dynamics in supercooled liquids (more than 15 orders of magnitude) upon a small change in temperature, as the glass transition temperature is approached.

Some recent theoretical approaches build upon ideas which were presented several decades ago [7–12]. In these works, the slowing down of the dynamics was connected to the presence of basins in configuration space. The short time dynamics (on a ps time scale) was related to the process of exploring a finite region of phase space around a local potential energy minimum, while the long time dynamics was connected to the transition among different local potential energy minima [10,12]. In this picture, upon cooling the intrabasin motion becomes more and more separated in time from the slow (and strongly T dependent) interbasin motion. The decrease of the entropy of supercooled liquids on cooling [8] was associated with the progressive ordering of the system in configuration space, i.e., in the progressive population of basins with deeper energy but of lower degeneracy [9].

Following these ideas, Stillinger and Weber [12] introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy hypersurface—maps to the same IS. This precise operational definition of a basin allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)

where \(R_{\alpha}\) is the set of points composing the basin \(\alpha\), \(\Phi_{\alpha}\) is the potential energy of 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. The integration over the momenta introduces the thermal wavelength \(\lambda = \sqrt{\beta h^2/(2\pi m)}\), where \(m\) is the mass. Equation (1) shows that both the IS energy and the entropy of supercooled liquids on cooling [8] was introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy surface. A basin in configuration space allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)

where \(R_{\alpha}\) is the set of points composing the basin \(\alpha\), \(\Phi_{\alpha}\) is the potential energy of 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. The integration over the momenta introduces the thermal wavelength \(\lambda = \sqrt{\beta h^2/(2\pi m)}\), where \(m\) is the mass. Equation (1) shows that both the IS energy and the entropy of supercooled liquids on cooling [8] was introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy surface. A basin in configuration space allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)

where \(R_{\alpha}\) is the set of points composing the basin \(\alpha\), \(\Phi_{\alpha}\) is the potential energy of 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. The integration over the momenta introduces the thermal wavelength \(\lambda = \sqrt{\beta h^2/(2\pi m)}\), where \(m\) is the mass. Equation (1) shows that both the IS energy and the entropy of supercooled liquids on cooling [8] was introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy surface. A basin in configuration space allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)

where \(R_{\alpha}\) is the set of points composing the basin \(\alpha\), \(\Phi_{\alpha}\) is the potential energy of 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. The integration over the momenta introduces the thermal wavelength \(\lambda = \sqrt{\beta h^2/(2\pi m)}\), where \(m\) is the mass. Equation (1) shows that both the IS energy and the entropy of supercooled liquids on cooling [8] was introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy surface. A basin in configuration space allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)

where \(R_{\alpha}\) is the set of points composing the basin \(\alpha\), \(\Phi_{\alpha}\) is the potential energy of 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. The integration over the momenta introduces the thermal wavelength \(\lambda = \sqrt{\beta h^2/(2\pi m)}\), where \(m\) is the mass. Equation (1) shows that both the IS energy and the entropy of supercooled liquids on cooling [8] was introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy surface. A basin in configuration space allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)

where \(R_{\alpha}\) is the set of points composing the basin \(\alpha\), \(\Phi_{\alpha}\) is the potential energy of 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. The integration over the momenta introduces the thermal wavelength \(\lambda = \sqrt{\beta h^2/(2\pi m)}\), where \(m\) is the mass. Equation (1) shows that both the IS energy and the entropy of supercooled liquids on cooling [8] was introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy surface. A basin in configuration space allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)

where \(R_{\alpha}\) is the set of points composing the basin \(\alpha\), \(\Phi_{\alpha}\) is the potential energy of 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. The integration over the momenta introduces the thermal wavelength \(\lambda = \sqrt{\beta h^2/(2\pi m)}\), where \(m\) is the mass. Equation (1) shows that both the IS energy and the entropy of supercooled liquids on cooling [8] was introduced the concept of inherent structure (IS), defined as the set of points that—via a steepest descent path along the potential energy surface. A basin in configuration space allows one to partition configuration space into an ensemble of nonoverlapping basins. Thus, the canonical partition function \(Z\) for a system of \(N\) atoms at inverse temperature \(\beta = 1/k_B T\) can be written as

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

(1)
in equilibrating atomic configurations at low \( T \). Only recently, Sastry et al. [15] addressed the problem of evaluating the \( T \) dependence of the average IS energy \( \langle \bar{\varepsilon}_{IS} \rangle \) in supercooled states in a binary mixture of Lennard-Jones particles, observing a significant decrease of \( \bar{\varepsilon}_{IS} \) on supercooling. This result, also observed for other models for liquids, e.g., in models for water [14] and orthoterenphenyl [16], furnishes strong evidence of the relevant role played by the low-energy basins on cooling. In a recent work [17], we proposed to invert the relation between the \( \bar{\varepsilon}_{IS} \) energy and \( T \) to define an effective temperature at which the configurational part of the system is in equilibrium. This hypothesis, which has been proven useful in interpreting the aging process in a model liquid in terms of progressive thermalization of the IS [17], supports the validity of Eq. (2) and, together with the work of Sastry et al., calls for an effort in the direction of checking the formal expression for the supercooled liquid free energy, i.e., the \( T \) range of validity, and an effort in the direction of evaluating the \( \bar{\varepsilon}_{IS} \) dependence of the configurational entropy. This article is a first effort in this direction.

The model system we study is the well-known 80-20 Lennard-Jones A-B binary mixture [18], composed of 1000 atoms in a volume \( V_0 = (9.4)^3 \). Units of length and energy are defined by the \( \sigma \) and \( \epsilon \) parameters of the A-A Lennard Jones interaction potential. The mass of atom \( A \) is chosen to be 1. In these units, \( k_B = 1 \). Simulations, covering the range \( 0.446 < T < 5 \), have been performed in the canonical ensemble by coupling the system to a Nose-Hoover thermostat. This system is well characterized and its slow dynamics has been studied extensively [18]. The critical temperature of mode coupling theory \( T_{MCT} \) for this system is 0.435 [18].

Between 500 and 1000 equilibrium configurations for each \( T \) (covering more than 80 million integration time steps for each \( T \)) have been quenched to their local minima by using a standard conjugate-gradient minimization algorithm. By performing this large number of quenches we are able to determine not only \( \bar{\varepsilon}_{IS} \) and its \( T \) dependence but also the probability distribution \( P(\varepsilon_{IS},T) \), shown in Fig. 1A.

In the \( T \) region where Eq. (4) is supposed to hold, curves of \( \ln[P(\varepsilon_{IS},T)] + \beta \varepsilon_{IS} \) are equal to \( S_{conf}(\varepsilon_{IS})/k_B - \beta f(\beta, \varepsilon_{IS}) \), except for the \( T \)-dependent constant \( \ln[Z(\beta)] \). If \( f(\beta, \varepsilon_{IS}) \) only has a weak dependence on \( \varepsilon_{IS} \), then it is possible to superimpose \( P(\varepsilon_{IS},T) \) curves at different temperatures which overlap in \( \varepsilon_{IS} \). The resulting \( \varepsilon_{IS} \)-dependent curve is, except for an unknown constant, \( S_{conf}(\varepsilon_{IS})/k_B \) in the \( \varepsilon_{IS} \) range sampled within the studied \( T \) interval. This procedure is displayed in Fig. 1B. We note that while below \( T = 0.8 \) curves for different \( T \) lie on the same master curve, curves for \( T > 0.8 \) have different \( \varepsilon_{IS} \) dependence, thus showing the progressive \( \varepsilon_{IS} \)=dependence of \( f(\beta, \varepsilon_{IS}) \). The overlap between different \( P(\varepsilon_{IS},T) \) curves below \( T = 0.8 \) indicates that the obtained master curve is indeed, except for an unknown constant, the \( \varepsilon_{IS} \) configurational entropy, i.e., the logarithm of the number of basins with the same \( \varepsilon_{IS} \) value.

It is particularly relevant that, for \( T < 0.8 \), \( f(\beta, \varepsilon_{IS}) \approx f(\beta) \) and thus \( Z \) [Eq. (2)] is well approximated by the product of a vibrational contribution \( [e^{-\beta \varepsilon}] \) and of a configurational contribution depending only on the IS energies and their degeneracy \( \int d\varepsilon_{IS} \Omega(\varepsilon_{IS}) e^{-\beta \varepsilon_{IS}} \). Thus the liquid can be considered as composed by two independent subsystems, respectively described by the IS and by the vibrational part. The IS subsystem can be considered as a continuum of levels characterized by an energy value \( \varepsilon_{IS} \) and an associated degeneracy \( \Omega(\varepsilon_{IS}) \). When the IS subsystem is in thermal equilibrium with the vibrational subsystem, then the \( T \) dependence of the

![FIG. 1. (a) Distributions \( P(\varepsilon_{IS},T) \) of the IS energy (per atom) for different temperatures \( T \). From left to right: \( T = 0.446, 0.466, 0.5, 0.55, 0.6, 0.8, 1.0, 2.0, \) and 4.0. (b) \( \ln[P(\varepsilon_{IS},T)] + \beta \varepsilon_{IS} + C(T) \), for different \( T \). The curves which do not lie on the continuous line correspond to \( T = 4.0, 2.0, 1.5, 1.0, \) and 0.8 (bottom to top). The constant \( C(T) \) has been chosen to maximize the overlap between curves with different \( T \) and the overlap with \( S_{conf}(\varepsilon_{IS}) \) (in absolute units) calculated from \( \Delta S(T) \), as discussed in the text. \( S_{conf}(\varepsilon_{IS}) \) is shown as a continuous line both in (b) and in the enlarged \( \varepsilon_{IS} \) range in (c). Note that, when \( \varepsilon_{IS} = -7.82, S_{conf} = 0 \).

3215
The average configurational entropy \( \tilde{S}_{\text{conf}} \) can be evaluated using the standard thermodynamic relation
\[
\frac{d \tilde{S}_{\text{conf}}(T)}{d \epsilon_{1S}} = \frac{1}{T},
\]  
(i.e., by integrating the \( T \) dependence of \( d \epsilon_{1S}/T \)).

While the evaluation of the \( T \) dependence of \( S_{\text{conf}} \) already furnishes relevant information, the evaluation of the unknown integration constant would allow for a determination of the number of IS with the same \( \epsilon_{1S} \) and, via a suitable low \( T \) extrapolation, to the determination of the so-called Kauzmann temperature \( T_K \), i.e., the \( T \) at which the configurational entropy appears to approach zero. To do so we exploit the fact that Eq. (2) predicts that the liquid free energy \( F_{\text{liquid}}(T) \) can be written as [19,20]
\[
F_{\text{liquid}}(T) = -k_B T \ln[Z(T)]
= \epsilon_{1S}(T) - T S_{\text{conf}}[\epsilon_{1S}(T)] + f[\beta, \epsilon_{1S}(T)],
\]  
where \( \epsilon_{1S}(T) \) is the \( \epsilon_{1S} \) value which maximizes the integrand in Eq. (2). We assume that at the lowest studied \( T \), the unknown \( f(\beta, \epsilon_{1S}) \) can be approximated by the harmonic free energy of a disordered system characterized by the eigenfrequencies spectrum calculated from the distribution of IS at the corresponding \( T \) [21]. In this approximation, the entropy of the liquid, which can be calculated via thermodynamic integration, minus the entropy of the corresponding harmonic disordered solid, provides an estimate of the configurational entropy in absolute units.

To calculate the liquid entropy we perform a thermodynamic integration first along the \( T = 5.0 \) isotherm, from infinite volume down to \( V_0 \), followed by a \( T \) integration of the specific heat at fixed volume, down to the lowest studied temperature. Since the \( T \) dependence of the potential energy \( E \) along the studied isochore is extremely well described by the law \( E(T) \sim T^{3/2} \), in agreement with theoretical predictions [22], the potential energy contribution to the liquid entropy follows the law \( T^{-2/5} \). By adding the kinetic energy contribution we obtain an analytic expression which can reliably be extrapolated to temperatures lower than the studied ones.

The evaluated \( T \) dependence of liquid and disordered-solid entropies is reported in Fig. 2. There we also show the contribution to the disordered-solid entropy arising from the \( T \) dependence of the eigenfrequencies spectrum, to confirm that the \( T \) dependence of the harmonic solid frequencies contributes only weakly to the entropy. The \( T \) dependence of \( \Delta S \equiv S_{\text{liquid}} - S_{\text{disordered-solid}} \) is shown in Fig. 3A. We note that this difference vanishes at \( T = 0.297 \pm 0.02 \), which defines \( T_K \) for the studied binary mixture. An independent recent estimate of \( T_K \) for this system, based on an integral equation approach and a similar analysis of simulation data, is \( T_K = 0.29 \) [23]. The resulting ratio between \( T_K \) and \( T_{\text{MCT}} \) supports the view that the studied system has intermediate fragility character, as recently predicted by Angell and co-workers [24].

At the lowest studied temperatures, where the harmonic approximation is valid [21], \( \Delta S \) coincides with \( S_{\text{conf}}(T) \). We use this identity to calculate the unknown integration constant for the inherent structure entropy. Moreover, by integrating \( T d[\Delta S(T)] \), both the configurational energy dependence of the configurational entropy (Fig. 1C) and the \( T \) dependence of the configurational energy (3B) can be evaluated, allowing one to bridge the gap between \( T_K \) and the lowest \( T \) at which we were able to equilibrate the system. The present analysis predicts \( \epsilon_{1S}(T_K) = -7.82 \pm 0.01 \). Thus, both the configuration entropy and energy around \( T_{\text{MCT}} \) is halfway between \( T_K \) and the high \( T \) value, suggesting that, at the lowest temperature which we have been able to equilibrate, the ordering process in configuration space is far from being complete.

The data reported in this article offer a quantitative thermodynamic analysis of the supercooling state. This picture confirms the fruitful ideas put forward a long time ago [8–12] and shows that a thermodynamic approach for the inherent structures subsystem becomes possible in supercooled states, since the thermodynamics of the inherent structures almost completely decouples from the "vibrational" thermodynamics. In particular, the quantitative evaluation of the degeneracy of the inherent structures [25] for a well characterized system constitutes a basis for
FIG. 3. Configurational entropy (a) and energy (b) as a function of $T$ calculated as differences of the liquid and disordered-solid entropies and energies, respectively. The arrow indicates $T_{\text{MCT}}$ for this system. The full circles in (b) are $\bar{e}_{IS}(T)$. Note that in the region where the harmonic approximation for the disordered solid is expected to be valid $21$, $\bar{e}_{IS}(T)$ coincides with the configurational energy.

a comprehensive description of the slow dynamics below $T_{\text{MCT}}$, the $T$ range in which an accurate theoretical prediction is still missing and for a microscopic understanding of the out-of-equilibrium thermodynamics [26].

We thank B. Coluzzi, G. Parisi, and P. Verrocchio for sharing with us their recent independent results of the BM LJ system ([23]). We thank G. Parisi for bringing to our attention Ref. [22]. We thank S. Ciuchi, A. Crisanti, K. Kawasaki, E. La Nave, P. Poole, A. Scala, and R. Speedy for comments. F.S. and P.T. acknowledge support from MURST PRIN and W.K. from the DFG through SFB 262.

[19] In going from Eq. (2) to Eq. (6) we have performed a maximum integrand evaluation of the partition function.
[21] Below $T = 0.5$, $e_{1S}(T) + \frac{3}{2}k_BT$ is close to the average potential energy, supporting the hypothesis that the system mainly probes an harmonic potential landscape.
[25] Previous estimates of the degeneracy of $e_{1S}$ were available only for systems composed by less than 50 atoms [27,28].