

Inherent Structure Entropy of Supercooled Liquids

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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.

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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 T , 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 *local* minimum configuration of the $3N$ -dimensional potential energy surface. A basin in configuration space was 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

$$Z = \lambda^{-3N} \sum_{\alpha} \exp(-\beta \Phi_{\alpha}) \int_{R_{\alpha}} \exp[-\beta \Delta_{\alpha}(\mathbf{r}^N)] d\mathbf{r}^N \quad (1)$$

where R_{α} is the set of points composing the basin α , Φ_{α} is the potential energy of 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. 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 thermal excitation within the basin region R_{α} contribute to Z . Stillinger and Weber also noted that, if the value of the potential energy minimum uniquely characterizes the properties of the basin, then a strong simplification of Eq. (1) can be performed. By introducing a density of states $\Omega(e_{IS})$ with IS energy e_{IS} , Z can be written as

$$Z \approx \int de_{IS} \Omega(e_{IS}) \exp[-\beta e_{IS} - \beta f(\beta, e_{IS})] \quad (2)$$

where

$$-\beta f(\beta, e_{IS}) = \ln \left(\int_{R(e_{IS})} \exp[-\beta \Delta_{e_{IS}}(\mathbf{r}^N)] \frac{d\mathbf{r}^N}{\lambda^{3N}} \right) \quad (3)$$

can be interpreted as free energy of the system when confined to one of the characteristic basins with IS energy e_{IS} . Then, the probability that a configuration of the liquid extracted from an equilibrium ensemble of configurations at temperature T is associated to an IS with energy between e_{IS} and $e_{IS} + \delta e_{IS}$ is

$$\begin{aligned} P(e_{IS}, T) &= \frac{\Omega(e_{IS}) \delta e_{IS} \exp[-\beta e_{IS} - \beta f(\beta, e_{IS})]}{Z(\beta)} \\ &= \frac{\exp[-\beta(e_{IS} - TS_{\text{conf}}(e_{IS}) + f(\beta, e_{IS}))]}{Z(\beta)} \end{aligned} \quad (4)$$

where we have defined $S_{\text{conf}}(e_{IS}) \equiv k_B \ln[\Omega(e_{IS}) \delta e_{IS}]$, since $\Omega(e_{IS}) \delta e_{IS}$ is the number of states between e_{IS} and $e_{IS} + \delta e_{IS}$.

The formalism proposed by Stillinger and Weber, although often used in the past to clarify structural issues in liquids [13,14], for a long time was not quantitatively applied to computer studies of the glass transition problem, due to the significant computational effort required

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 (\bar{e}_{IS}) in supercooled states in a binary mixture of Lennard-Jones particles, observing a significant decrease of \bar{e}_{IS} on supercooling. This result, also observed for other models for liquids, e.g., in models for water [14] and orthoterphenyl [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{e}_{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 e_{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 σ and ϵ 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{e}_{IS} and its T dependence but also the probability distribution $P(e_{IS}, T)$, shown in Fig. 1A.

In the T region where Eq. (4) is supposed to hold, curves of $\ln[P(e_{IS}, T)] + \beta e_{IS}$ are equal to $S_{conf}(e_{IS})/k_B - \beta f(\beta, e_{IS})$, except for the T -dependent constant $\ln[Z(\beta)]$. If $f(\beta, e_{IS})$ has only a weak dependence on e_{IS} , then it is possible to superimpose $P(e_{IS}, T)$ curves at different temperatures which overlap in e_{IS} . The resulting e_{IS} -dependent curve is, except for an unknown constant, $S_{conf}(e_{IS})/k_B$ in the e_{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 e_{IS} dependence, thus showing the progressive e_{IS} dependence of $f(\beta, e_{IS})$. The overlap between different $P(e_{IS}, T)$ curves below $T = 0.8$ indicates that the obtained master curve is indeed, except for

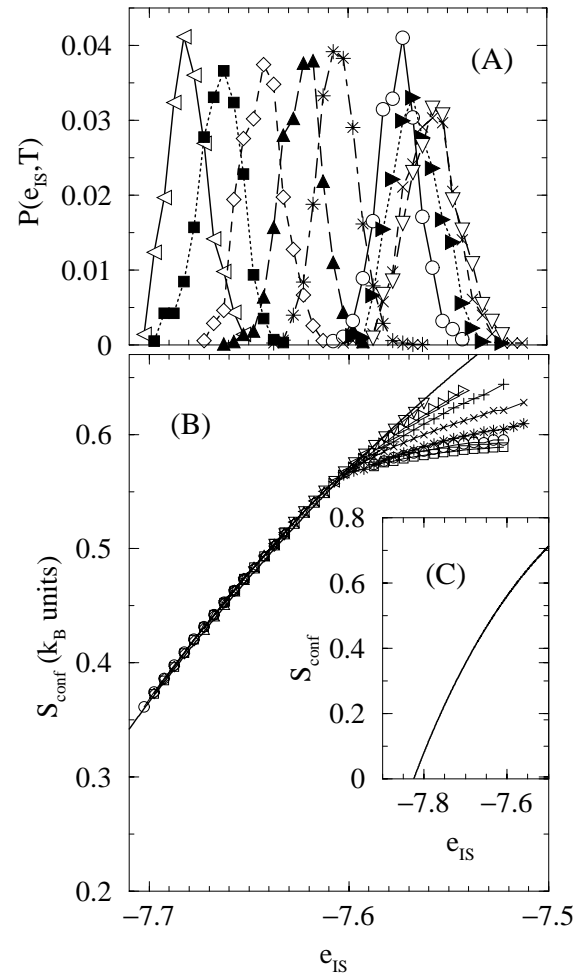


FIG. 1. (a) Distributions $P(e_{IS}, T)$ of the IS energy (per atom) for different temperatures T . From left to right: $T = 0.446, 0.466, 0.5, 0.55, 0.6, 0.8, 1.0, 2.0,$ and 4.0 . (b) $\ln[P(e_{IS}, T)] + \beta e_{IS} + C(T)$, for different T . The curves which do not lie on the continuous line correspond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

an unknown constant, the e_{IS} configurational entropy, i.e., the logarithm of the number of basins with the same e_{IS} value.

It is particularly relevant that, for $T < 0.8$, $f(\beta, e_{IS}) \approx f(\beta)$ and thus Z [Eq. (2)] is well approximated by the product of a vibrational contribution [$e^{-\beta f}$] and of a configurational contribution depending only on the IS energies and their degeneracy [$\int de_{IS} \Omega(e_{IS}) e^{-\beta e_{IS}}$]. 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 e_{IS} and an associated degeneracy $\Omega(e_{IS})$. When the IS subsystem is in thermal equilibrium with the vibrational subsystem, then the T dependence of the

average configurational entropy \bar{S}_{conf} can be evaluated using the standard thermodynamic relation

$$\frac{d\bar{S}_{\text{conf}}(T)}{d\bar{e}_{\text{IS}}} = \frac{1}{T}, \quad (5)$$

i.e., by integrating the T dependence of $d\bar{e}_{\text{IS}}/T$.

While the evaluation of the T dependence of S_{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 e_{IS} 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]

$$\begin{aligned} F_{\text{liquid}}(T) &= -k_B T \ln[Z(T)] \\ &= \bar{e}_{\text{IS}}(T) - TS_{\text{conf}}[\bar{e}_{\text{IS}}(T)] + f[\beta, \bar{e}_{\text{IS}}(T)] \end{aligned} \quad (6)$$

where $\bar{e}_{\text{IS}}(T)$ is the e_{IS} value which maximizes the integrand in Eq. (2). We assume that at the lowest studied T , the unknown $f(\beta, \bar{e}_{\text{IS}})$ 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 $E(T) \sim T^{3/5}$, 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 on a similar analysis of simulation data, is $T_K = 0.29$ [23]. The resulting ratio between T_K and T_{MCT} supports the view that

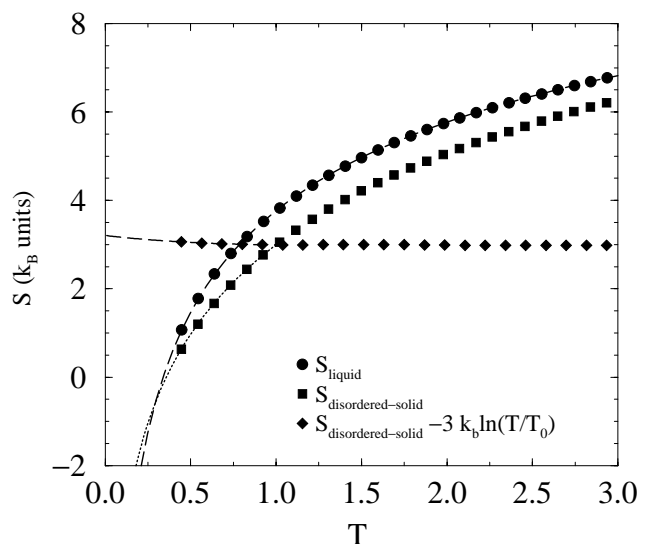


FIG. 2. Disordered-solid (filled squares) and liquid (filled circles) entropies as a function of T . Filled diamonds are $S_{\text{disordered-solid}} - 3k_B \ln(T/T_0)$, with $T_0 = 1$, to demonstrate the weakness of the T contribution arising from the T dependence of frequency distribution. Below $T = 1$, this weak T -dependent contribution is fitted well (long-dashed line) by the quadratic polynomial $3201.62309 - 402.760885T + 199.228407T^2$, providing a reliable extrapolation of $S_{\text{disordered-solid}}$ to T lower than the studied ones (dotted line). The liquid entropy is extrapolated according to the theoretical predictions discussed in Ref. [22], i.e., $S_{\text{liquid}} + 1.5k_B \ln(T/T_0) \sim T^{-2/5}$.

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], ΔS coincides with $S_{\text{conf}}(T)$. We use this identity to calculate the unknown integration constant for the inherent structure entropy. Moreover, by integrating $Td[\Delta S(T)]$, 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 $e_{\text{IS}}(T_K) = -7.82 \pm 0.01$. Thus, both the configuration entropy and energy around T_{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

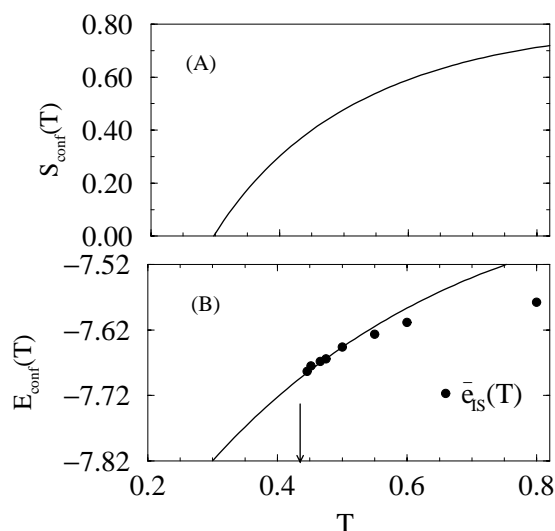


FIG. 3. Configurational entropy (a) and energy (b) as a function of T calculated as differences of the liquid and disordered-solid entropies and energies, respectively. The arrow indicates T_{MCT} for this system. The full circles in (b) are $\bar{e}_{1S}(T)$. Note that in the region where the harmonic approximation for the disordered solid is expected to be valid [21], $\bar{e}_{1S}(T)$ coincides with the configurational energy.

a comprehensive description of the slow dynamics below T_{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].

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- [1] For a recent review, see articles in *Science* **267**, (1995), and M.D. Ediger, C.A. Angell, and S.R. Nagel, *J. Phys. Chem.* **100**, 13 200 (1996).
- [2] W. Götze, *J. Phys. Condens. Matter* **11**, A1 (1999).
- [3] M. Mezard and G. Parisi, *J. Phys. Condens. Matter* **11**, A157 (1999), and references therein; M. Mezard, *Physica (Amsterdam)* **265A**, 352 (1999); B. Coluzzi, M. Mezard, G. Parisi, and P. Verrocchio, *cond-mat/9903129*; M. Mezard and G. Parisi, *cond-mat/9812180*.
- [4] R. Speedy, *J. Phys. Condens. Matter* **10**, 4185 (1998); **9**, 8591 (1997); **8**, 10907 (1996); *J. Phys. Chem. B* **103**, 4060 (1999).
- [5] See, e.g., *Proceedings of the Third International Discussion Meeting* [*J. Non-Cryst. Solids* **235–237** (1998)].

- [6] K. Binder *et al.*, in *Complex Behaviour of Glassy Systems*, edited by M. Rubí and C. Perez-Vicente (Springer-Verlag, Berlin, 1997), p. 22.
- [7] R.O. Davies and G.O. Jones, *Adv. Phys.* **2**, 370 (1953).
- [8] A. W. Kauzmann, *Chem. Rev.* **43**, 219 (1948).
- [9] G. Adams and J. H. Gibbs, *J. Chem. Phys.* **43**, 139 (1958); J. H. Gibbs and E. A. Di Marzio, *J. Chem. Phys.* **28**, 373 (1958).
- [10] M. Goldstein, *J. Chem. Phys.* **51**, 3728 (1969).
- [11] E. A. Di Marzio and A. J. Yang, *J. Res. Natl. Inst. Stand. Technol.* **102**, 135 (1997), and references therein.
- [12] F.H. Stillinger and T.A. Weber, *Phys. Rev. A* **25**, 978 (1982); *Science* **225**, 983 (1984); F.H. Stillinger, *Science* **267**, 1935 (1995).
- [13] T.A. Weber and F.H. Stillinger, *J. Chem. Phys.* **87**, 3252 (1987); F. Sciortino, A. Geiger, and H.E. Stanley, *Nature (London)* **354**, 218 (1991); *Phys. Rev. Lett.* **65**, 3452 (1990).
- [14] I. Ohmine, H. Tanaka, and P. G. Wolynes, *J. Chem. Phys.* **89**, 5852 (1988); H. Tanaka, *Nature (London)* **380**, 328 (1996).
- [15] S. Sastry, P.G. Debenedetti, and F.H. Stillinger, *Nature (London)* **393**, 554 (1998). See also the related work of H. Jonsson and H.C. Andersen, *Phys. Rev. Lett.* **60**, 2295 (1988).
- [16] F. Sciortino, S. Sastry, and P. Tartaglia, *cond-mat/9805040*.
- [17] W. Kob, F. Sciortino, and P. Tartaglia, *cond-mat/9905090*.
- [18] W. Kob and H.C. Andersen, *Phys. Rev. E* **51**, 4626 (1995); **52**, 4134 (1995); M. Nauroth and W. Kob, *ibid.* **55**, 675 (1997); T. Gleim, W. Kob, and K. Binder, *Phys. Rev. Lett.* **81**, 4404 (1998).
- [19] In going from Eq. (2) to Eq. (6) we have performed a maximum integrand evaluation of the partition function.
- [20] F.H. Stillinger, *J. Phys. Chem. B* **102**, 2807 (1998).
- [21] Below $T = 0.5$, $e_{1S}(T) + \frac{3}{2}k_B T$ is close to the average potential energy, supporting the hypothesis that the system mainly probes an harmonic potential landscape.
- [22] Y. Rosenfeld and P. Tarazona, *Mol. Phys.* **95**, 141 (1998).
- [23] B. Coluzzi, P. Verrocchio, P. Mezard, and G. Parisi, *cond-mat/9904124*.
- [24] C.A. Angell, B.E. Richards, and V. Velikov, *J. Phys. Condens. Matter* **11**, A75 (1999), and references therein.
- [25] Previous estimates of the degeneracy of e_{1S} were available only for systems composed by less than 50 atoms [27,28].
- [26] Th. M. Nieuwenhuizen, *Phys. Rev. Lett.* **80**, 5580 (1998); **79**, 1317 (1997); L.F. Cugliandolo, J. Kurchan, and L. Peliti, *Phys. Rev. E* **55**, 3898 (1997).
- [27] A. Heuer, *Phys. Rev. Lett.* **78**, 4051 (1997). See also for the same model, F.H. Stillinger and T.A. Weber, *Phys. Rev. A* **28**, 2408 (1983).
- [28] L. Angelani, G. Parisi, G. Ruocco, and G. Vilianni, *Phys. Rev. Lett.* **81**, 4648 (1998).