

Inherent structures and Kauzmann temperature of confined liquidsA. Attili,¹ P. Gallo,^{1,2,*} and M. Rovere^{1,2}¹*Dipartimento di Fisica, Università "Roma Tre," Via della Vasca Navale 84, 00146 Roma, Italy*²*INFN Roma Tre and Democritos National Simulation Center, Via della Vasca Navale 84, 00146 Roma, Italy*

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Calculations of the thermodynamical properties of a supercooled liquid confined in a matrix are performed with an inherent structure analysis. The liquid entropy is computed by means of a thermodynamical integration procedure. The contributions to the free energy of the liquid can be decoupled also in confinement in the configurational and the vibrational parts. We show that the vibrational entropy can be calculated in the harmonic approximation as in the bulk case. The Kauzmann temperature of the confined system is estimated from the behavior of the configurational entropy.

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I. INTRODUCTION

It is well known that most liquids upon supercooling undergo a transition to an amorphous state, where mechanical properties typical of a solid phase combine with a microscopically disordered structure [1–4]. Just below the melting temperature the supercooled liquids manifest a slowing down of dynamics. This behavior has been successfully interpreted in terms of the mode coupling theory (MCT) which is able to predict the asymptotic properties of the density correlators upon decreasing temperature on approaching a temperature T_C [5]. This temperature marks a crossover from a region where the exploration of the phase space of the system is determined by structural relaxations, to a region where it is determined by hopping processes. In the last few years theoretical approaches based on the analysis of the potential energy landscape (PEL) of the supercooled liquid have driven significant progress in the study of the thermodynamics of the glass transition below T_C [4,6–16].

The phenomena related to the glass transition are yet not well understood in the case of liquids in confined geometries or at contact with solid surfaces although these situations are very relevant for many technological and biological applications. It is in fact still not clear how the theoretical approaches developed for bulk supercooled liquids can be extended to describe the corresponding phenomenology when liquids are confined.

While it has been shown that MCT works also for interpreting the dynamics of confined liquids in several cases [17–21], no studies of dynamics in confinement below T_C have so far been performed. It is therefore very relevant to study how the PEL and the thermodynamical properties below T_C are modified by the presence of confinement. Recently a mean field analysis of the PEL for thin films has shown that confinement could affect the thermodynamical behaviour and the glass transition [22].

As proposed by different authors [23,24] the behavior of a bulk supercooled liquid is determined by the dynamics of the system in and between the basins of the PEL. At low enough

temperature there are two separated regimes; the dynamics on the short time scale can be described as the motion around the local minima, while the long time dynamics is related to the transition between different basins of energy. This separation of regimes has been framed by Stillinger and Weber (SW) [24] in the formalism of the inherent structure (IS). According to their definition an IS is the configuration of local minima of the PEL. A basin is the set of points that maps to the same IS under a local energy minimization performed by a steepest descent procedure starting from a configuration equilibrated at a certain temperature. In the SW formulation under the assumption that the basins with the same IS energy e_{IS} have equivalent properties in the canonical partition function, the motions between different basins and the vibrations inside a single basin can be decoupled. This formulation allows one to define and study a configurational entropy S_{conf} . This quantity, which represents the difference between the liquid and the disordered solid entropies, plays a central role in understanding the glass transition.

In the process of cooling the configurational entropy decreases and eventually vanishes at a finite temperature, defined as the Kauzmann temperature T_K [25]. In the interpretation of Adam, Gibbs, and Di Marzio [26–28] at T_K an ideal thermodynamical transition should take place from the supercooled liquid to an amorphous phase with a single configuration [4,9,12,28–30]. The singular behavior of thermodynamical quantities measured in experiments at the conventional glass transition temperature T_g would be related to the true transition occurring at $T_K < T_g$.

It is generally found that phase transitions in confined fluids are modified by confinement from both geometric effects and the interaction with the substrate. This is particularly true when large spatial correlations are expected to take place and finite size effects could influence the transition in a fluid confined in a restricted environment. This would also be the case for the glass transition at T_K if it is interpreted in terms of a second-order phase transition [31] or in the framework on the mosaic state scenario [33].

Here we consider the case of a glass forming confined liquid, a Lennard-Jones binary mixture (LJBM), embedded in a disordered array of soft spheres. Molecular dynamics simulations have been performed for this system upon cooling and a numerical test of MCT properties has been carried

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out. The mixture follows in this confining environment also, as in the bulk, MCT predictions very well [17,18]. Nonetheless important differences due to confinement are found. In particular the range of validity of the MCT predictions suffers a reduction of 60% with respect to the bulk. We found a crossover temperature $T_C=0.356$ (in Lennard-Jones units) to be compared with the bulk value $T_C=0.435$ (in Lennard-Jones units) [33] and therefore we observed a reduction of circa 20% of T_C in going from the bulk to the confined LJBM.

We performed in this paper an IS analysis to evaluate the IS distributions, the temperature dependence of the configurational entropy, and finally the Kauzmann temperature of the confined LJBM to be compared with the corresponding values for the LJBM in the bulk phase [7,12]. The paper develops as follows. In the next section we report computational details. The third section is devoted to the calculation of the IS for the confined LJBM. In the fourth section we evaluate the configurational entropy and the Kauzmann temperature. The last section is devoted to the conclusions.

II. COMPUTER SIMULATION OF THE CONFINED LIQUID UPON SUPERCOOLING

We studied the LJBM proposed in Ref. [33] embedded in a rigid disordered array of 16 soft spheres. The liquid binary mixture is composed by 800 particles of type *A* and 200 particles of type *B*. The parameters of the Lennard-Jones potential are $\epsilon_{AA}=1$, $\sigma_{AA}=1$, $\epsilon_{BB}=0.5$, $\sigma_{BB}=0.88$, $\epsilon_{AB}=1.5$, and $\sigma_{AB}=0.8$. In the following, LJ units will be used. The *A* and *B* particles interact with the soft spheres with a potential $V(r)=\epsilon(\sigma/r)^{12}$ where $\epsilon_{SA}=0.32$, $\sigma_{SA}=3$, $\epsilon_{SB}=0.22$, $\sigma_{SB}=2.94$.

Molecular dynamics (MD) simulations have been performed in the *NVT* ensemble along an isochoric path at various temperatures upon cooling. The box length is fixed to $L=12.6$. In previous work we already investigated the system in the range of temperature from $T=5.0$ to 0.37 and further MD simulation details are reported in Refs. [17,18].

Starting from the equilibrated configurations at the temperatures $T=5, 2, 0.8, 0.6, 0.55, 0.5, 0.475, 0.45, 0.425, 0.38$, we performed new simulations for each temperature in order to obtain a number of equally spaced configurations and calculate the corresponding IS for each temperature.

The ISs have been obtained by the conjugate gradient minimization procedure described in the literature and adapted to our confined system. For each temperature 1000 configurations have been minimized. The Hessian matrix has been diagonalized at each IS to calculate the eigenfrequencies.

III. INHERENT STRUCTURE ANALYSIS

In the SW formulation of IS the canonical partition function can be written as follows:

$$Z_N(T) = \int de_{IS} \Omega(e_{IS}) \exp\{-[e_{IS} + f(T, e_{IS})]/k_B T\} \quad (1)$$

where $\Omega(e_{IS})$ is the number of distinct basins with energy e_{IS} and $f(T, e_{IS})$ is the free energy of the system restricted to a

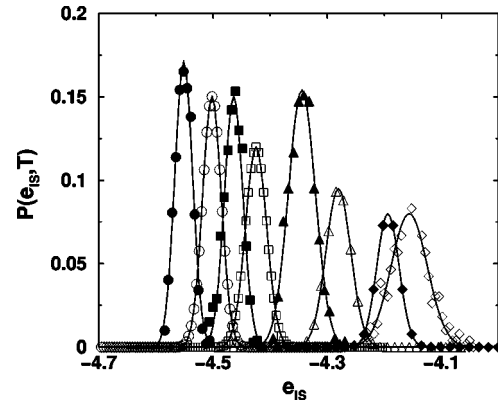


FIG. 1. Distribution functions $P(e_{IS}, T)$. Lower temperatures are on the left. The functions are omitted for temperatures $T=0.50$ and 0.55 since they are almost superimposed on the ones at $T=0.475$ and 0.60 , respectively.

single basin with energy e_{IS} . The configurational entropy S_{conf} can be defined as $S_{conf}=k_B \ln[\Omega(e_{IS})]$. The energies of the IS are distributed with a probability given by

$$P(e_{IS}, T) = \frac{\exp\{-[e_{IS} + f(T, e_{IS}) - TS_{conf}(e_{IS})]/k_B T\}}{Z_N(T)}. \quad (2)$$

The configurational entropy can be defined also as the difference between the liquid entropy and the entropy of the disordered solid (DS)

$$S_{conf} = S_{liquid} - S_{DS}. \quad (3)$$

From the quenches performed at each temperature we calculate the distribution functions $P(e_{IS}, T)$ of the IS. These are shown in Fig. 1 together with Gaussian best fits. The Gaussian curves appear to reproduce sufficiently well the distribution functions. For the lowest temperatures the curves are narrower and more peaked around the average value.

We can now look at the behavior of the configurational entropy by considering Eq. (2), from which we obtain

$$\begin{aligned} \ln[P(e_{IS}, T)] + e_{IS}/k_B T \\ = S_{conf}(e_{IS})/k_B - f(T, e_{IS})/k_B T - \ln[Z_N(T)]. \end{aligned} \quad (4)$$

The left-hand side of this equation can be calculated from the distribution functions of Fig. 1 to obtain a new set of curves. By plotting all these curves as function of e_{IS} we see that they can be superimposed by subtracting a temperature dependent term as shown in Fig. 2 for $T < 0.80$. Looking at the right hand side of Eq. (4) this result implies that the basin free energy $f(T, e_{IS})$ is almost independent of the IS energy. The master curve represents, apart from an unknown temperature dependent term, the configurational entropy.

Since the basin free energy is approximately independent of e_{IS} for $T < 0.8$ in the confined liquid, the partition function defined in Eq. (1) can be separated as

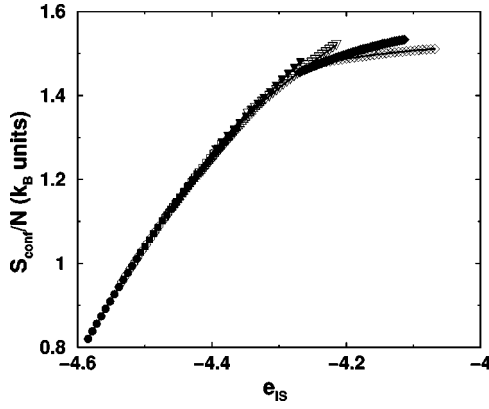


FIG. 2. Entropy per particle calculated from the distribution functions of the inherent structure energy according to Eq. (4) at the different temperatures $T=0.38, 0.425, 0.45, 0.475, 0.50, 0.55, 0.60, 0.80, 2.0, 5.0$. The unknown temperature dependent term is obtained by maximizing the overlap between the curves. For $T > 0.80$ the curves deviate from the master curve.

$$Z_N(T) \approx \exp[-f(T, e_{IS})/k_B T] \int de_{IS} \Omega(e_{IS}) \exp(-e_{IS}/k_B T). \quad (5)$$

The confined liquid at low enough temperature can be assumed to be composed of an inherent structure subsystem in thermal equilibrium with the vibrational subsystem. The IS represents the long time dynamics of the system due to transitions between the different basins of energy, whose degeneracy is counted by $\Omega(e_{IS}) = \exp(S_{conf}/k_B T)$. The vibrational spectrum is related to the oscillations close to the minimum of the single basin. It can be obtained by diagonalizing the Hessian matrix after a conjugate gradient minimization starting from equivalent state points [34].

In Fig. 3 we report the comparison of the density of state (DOS) of the vibrational spectrum of the confined and the bulk LJBM obtained with the same method. We observe that the confinement does not induce large changes in either the shape on the spectral range of the eigenfrequencies. For the bulk LJBM it has been also shown that the basin free energy can be approximated by the harmonic vibrational contribution [7]. We will come back later to this point.

IV. CONFIGURATIONAL ENTROPY AND KAUZMANN TEMPERATURE

The behavior of the configurational entropy has been determined from Eq. (4) and shown in Fig. 2 but the calculation of the Kauzmann temperature requires the absolute value of S_{conf} .

A thermodynamical integration procedure allows one to evaluate the full entropy of the liquid including the temperature dependent integration constant which appears in Eq. (4). Starting from a state reference point at temperature T_r at the given volume V of the simulation box, the entropy S_{tot} can be computed as

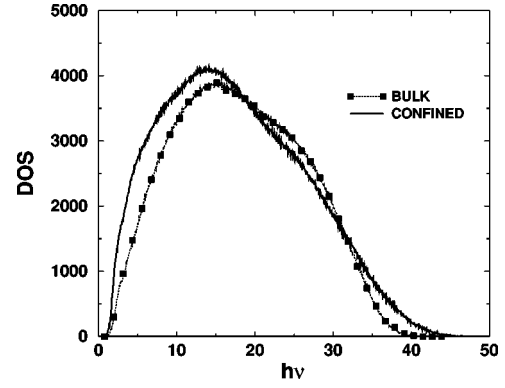


FIG. 3. Density of states of the confined liquid compared with the DOS of the bulk liquid. The DOSs are obtained by quenching the systems from $T=0.38$ for the confined mixture and from $T=0.51$ for the bulk. Both systems were equilibrated at the same pressure before the quench; the temperatures are different due to the fact that T_C is lower for the confined system [34].

$$S_{tot}(T, V) = S_{ref}(T_r, V) + \int_{T_r}^T \left(\frac{\partial U(T')}{\partial T'} \right)_V dT' \quad (6)$$

where $U(T)$ is the internal energy calculated in the simulation along the isochoric path. As reference point we assume $T_r=5.0$. The reference entropy $S_{ref}(T_r, V)$ is derived from the corresponding $S_{bulk}(T_r, V)$ of the bulk system at the same temperature T_r and volume V by adding the contribution of

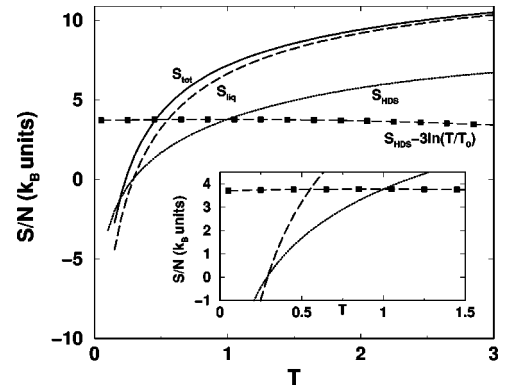


FIG. 4. Total entropy of the confined system as obtained from the thermodynamical integration (full line) as a function of T . The dashed curve is the entropy S_{liq} obtained after subtracting the contribution due to W_{conf} ; see Eq. (9). In the figure are also reported the vibrational entropy S_{HDS} (dotted line) calculated in the harmonic approximation and the quantity $S_{HDS} - 3 \ln(T/T_0)$ (broken line with filled squares) fitted with the polynomial $3.704 + 0.1555T - 0.0835T^2$. In the inset S_{liq} and S_{HDS} are reported on a larger scale to better show the crossing point corresponding to the Kauzmann temperature T_K . All entropies are per particle and in units of k_B .

the work needed to include the soft spheres by keeping the volume constant:

$$S_{ref}(T_r, V) = S_{ref}^{bulk}(T_r, V) + \frac{1}{T} [U(T_r, V) - U_{bulk}(T_r, V)]. \quad (7)$$

$S_{bulk}(T_r, V)$ is obtained as follows:

$$S_{ref}^{bulk}(T_r, V) = S_{ideal}^{bulk}(T_r, V) + \frac{U_{bulk}(T_r, V)}{T_r} + \int_{\infty}^V \frac{P_{exc}^{bulk}}{T_r} dV' \quad (8)$$

where P_{exc}^{bulk} is the excess pressure of the bulk and $S_{ideal}^{bulk}(T_r, V)$ is the entropy of the ideal two-component gas.

The result is the topmost curve shown in Fig. 4. Below the lowest investigated temperature $T=0.38$ the curve is extrapolated by an accurate polynomial fit.

At variance with the bulk in our case, the effective density of the confined liquid is not constant, since the free volume accessible to the A and B particles changes with the temperature due to the soft sphere interaction potential [17,18,34]. The calculation of S_{tot} has been performed along an isochoric path and the internal energy of the confined liquid used in Eq. (6) contains also a contribution $W_{conf}(T)$ due to the work done to change the effective density of the liquid inside the simulation box at constant volume. This contribution has to be subtracted to extract the entropy of the liquid from which the the configurational entropy can be obtained:

$$S_{liq}(T, V) = S_{tot}(T, V) - \int_{T_r}^T \frac{1}{T'} \left(\frac{\partial W_{conf}}{\partial T'} \right)_V dT'. \quad (9)$$

This integral can be calculated by referring to a corresponding bulk system simulated at the same pressures and temperatures of the confined mixture, by considering

$$\frac{\partial W_{conf}}{\partial T} = \frac{\partial W_{conf}}{\partial V_{liq}} \frac{\partial V_{liq}}{\partial T} \quad (10)$$

where V_{liq} is the effective volume of the confined liquid. $V_{liq}(T)$ can be derived by comparison with an equivalent bulk at the same pressure. The thermodynamical path followed by the equivalent bulk and the corresponding densities will be published in a separate paper [34]. The result for S_{liq} is also reported in Fig. 4. We note that S_{liq} of the confined system when compared to that of the bulk [7,12] assumes higher values for high temperatures but approaches the zero value at approximatively the same temperature as in the bulk. Therefore the enhancement of entropy due to the additional disorder induced by the presence of the soft spheres seems to become less marked as the temperature is decreased.

Assuming the harmonic approximation to be valid also for our confined LJBM, from the eigenfrequencies obtained from the IS we can evaluate the entropy of the harmonic disordered solid (HDS) with the formula

$$S_{HDS} = \sum_{i=1}^{3N-3} [1 - \ln(\beta \hbar \omega_i)]. \quad (11)$$

The result is also reported in Fig. 4. In the same figure is shown the quantity $S_{HDS}/Nk_B - 3 \ln(T/T_0)$, where $T_0=1$ has

been chosen as a reference temperature. It has a very weak T dependence well fitted by a quadratic polynomial. This shows that almost all the T dependence of the entropy S_{HDS} is contained in the term independent of the frequency distribution.

With the assumptions done for the vibrational spectrum of the basins we can identify the S_{HDS} with the entropy of the disordered solid S_{DS} . In this way the configurational entropy S_{conf} is obtained from the difference

$$S_{conf} \approx S_{liq} - S_{HDS}. \quad (12)$$

From Fig. 4, as best evident in the enlargement, we find that $S_{conf}=0$ at the temperature $T=0.292 \pm 0.02$ which can be identified as the Kauzmann temperature of the confined LJBM.

V. DISCUSSION AND CONCLUSIONS

We have shown that for a LJBM the IS analysis can be performed also in confinement. The absolute value of the entropy of the confined liquid can be obtained by thermodynamical integration by means of a procedure where one refers to an equivalent bulk system at the same temperature and volume as the confined liquid for including the ideal terms. The result must be corrected for the work done to change the density of the confined liquid keeping constant the volume of the simulation cell. The correction is calculated by comparison with a bulk liquid at the same pressure as the confined one. The combination of the IS analysis and the thermodynamical integration technique allows one to determine the Kauzmann temperature T_K of the system defined as the temperature at which the configurational entropy vanishes.

With the entropy of the disordered solid calculated in the harmonic approximation as in the bulk, we found that $T_K=0.292$ for the confined system to be compared with $T_K=0.297$ for the bulk. We observe therefore only a slight decrease of T_K upon confinement while a much more marked decrease is instead detected for the MCT crossover temperature T_C . We obtained in fact $T_C=0.356$ in confinement against $T_C=0.435$ in the bulk [18,34].

These results seem to confirm the connection between dynamics and the thermodynamic energy landscape sampling as a function of temperature [4]. In the region close to T_C the system is still at relatively high temperature. The ergodicity is assured by structural relaxations that require cooperative rearrangement of large portions of the liquid. This corresponds in the PEL picture to a system that has sufficient kinetic energy to sample a large portion of the PEL. In this region the modification to the PEL induced by the presence of the soft sphere matrix exerts a strong influence on the particle motions modifying substantially not only the T_C but also the critical exponents of the theory [17,18]. On approaching the Kauzmann temperature the system becomes trapped in a single minimum. In this situation only a small fraction of particles explores the configuration regions occupied by the soft sphere potential.

The confining matrix used in the present simulation mimics the connected pore structure of systems with high poros-

ity like silica xerogels. It appears that the confinement in this kind of system does not shift the thermodynamical liquid-glass transition but changes the way in which the configurational entropy approaches the limiting Kauzmann temperature. Further investigations will be necessary to understand (i) if the different behavior of S_{conf} implies modifications of the PEL, and (ii) if and how changes of porosity and/or size

of the confining spheres could modify the Kauzmann temperature.

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