Inherent Structures and Kauzmann Temperature of Confined Liquids

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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 part. 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, 2, 3, 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 \( T_C \). 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 a significant progress in the study of the thermodynamics of the glass transition below \( T_C \) [5, 6, 7, 8, 9, 10, 11, 12].

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 [13, 14, 15, 20, 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 structures (IS). According to their definition an IS is the configuration of local minima of the PEL. A basin is the set of points which 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 the Kauzmann temperature \( T_K \) [25]. In the interpretation of Adam, Gibbs and Di Marzio [20, 21] at \( T_K \) an ideal thermodynamical transition should take place from the supercooled liquid to an amorphous phase with a single configuration. 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 both from 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 be also the case for the glass transition at $T_K$ if it is interpreted in terms of a second order phase transition or in the framework of the mosaic state scenario.

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 out. The mixture follows also in this confining environment, 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 $T_C = r \cdot 356$ (in Lennard-Jones units) to be compared with the bulk value $T_C = 0.435$ (in Lennard-Jones units) 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. The last section is devoted to the conclusions. This would be also the case for the glass transition $C = 0.475$ (in Lennard-Jones units) to be compared with the bulk value $C = 0$.

II. COMPUTER SIMULATION OF THE CONFINED LIQUID UPON SUPERCOOLING

We studied the LJBM proposed in ref. \[38\] 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 $\epsilon_{AB} = 0.8$. In the following the 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 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 $T = 0.37$ and further MD simulation details are reported in ref. \[17, 18\].

Starting from the equilibrated configurations at the following 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 IS 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:

$$Z_N(T) = \int d\epsilon_{IS} \Omega(\epsilon_{IS}) \exp\left(-[\epsilon_{IS} + f(T, \epsilon_{IS})]/k_BT\right)$$ (1)

where $\Omega(\epsilon_{IS})$ is the number of distinct basins with energy $\epsilon_{IS}$ and $f(T, \epsilon_{IS})$ is the free energy of the system restricted to a single basin with energy $\epsilon_{IS}$. The configurational entropy $S_{conf}$ can be defined as $S_{conf} = k_B \ln(\Omega(\epsilon_{IS}))$. The energies of the IS are distributed with a probability given by

$$P(\epsilon_{IS}, T) = \frac{\exp[-(\epsilon_{IS} + f(T, \epsilon_{IS}) - TS_{conf}(\epsilon_{IS})]/k_BT]}{Z_N(T)}$$ (2)

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

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

From the quenches performed at each temperature we calculate the distribution functions $P(\epsilon_{IS}, T)$ 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

$$ln[P(\epsilon_{IS}, T)] + \epsilon_{IS}/k_BT = \frac{S_{conf}(\epsilon_{IS})}{k_B} - f(T, \epsilon_{IS})/k_BT - \ln[Z_N(T)]$$ (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 $\epsilon_{IS}$ we see that they can be superimposed by subtracting a temperature dependent term as shown in Fig. 2 for $T < 0.8$. Looking at the right hand side of Eq. 4 this result implies that the the basin free energy $f(T, \epsilon_{IS})$ is almost independent of the IS energy. The master curve represents, apart from an unknown temperature dependent term, the configurational entropy.
III. INTRINSIC STRUCTURE ENERGIES

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

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

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

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.

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 both the shape and the spectral range of the eigenfrequencies. For the bulk LJBM it has been also shown that the basin free energy can be approximated with the harmonic vibrational contribution. We will come back later to this point.

IV. CONFIGURATIONAL ENTROPY AND KAUSZMANN 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

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

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

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

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

$$S_{ref}(T_r, V) = S_{ideal}(T, V) + \frac{U_{bulk}(T, V)}{T} + \int_{V}^{V} \frac{p_{exc}}{T_{r}} dV' \quad (8)$$

where $p_{exc}$ is the excess pressure of the bulk and $S_{ideal}(T, V)$ 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 spheres interaction potential [12, 13, 14]. 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 configurational entropy can be obtained

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

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

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

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 [31]. 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 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 LJIBM, from the eigenfrequencies obtained from the IS we can evaluate the entropy of the harmonic disordered solid (HDS) with the formula

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

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

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

From Fig. 4 as best evident in the blow up, 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 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 cross-over temperature $T_C$. We obtained in fact $T_C = 0.356$ in confinement against $T_C = 0.435$ in the bulk \cite{18, 34}.

These results seem to confirm the connection between dynamics and the thermodynamics energy landscape sampling as a function of temperature \cite{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 \cite{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 spheres potential.

The confining matrix used in the present simulation mimics the connected pore structure of systems with high porosity 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, (ii) if and how changes of porosity and/or size of the confining spheres could modify the Kauzmann temperature.

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J. Phys. Chem. 105, 11809 (2001).
[30] B. Coluzzi, G. Parisi and P. Verrocchio, J. Chem. Phys. 112, 2933 (2000).
[31] L. Berthier, Phys. Rev. E 69, 020201(R) (2004).
[32] J. P. Bouchaud and G. Biroli, J. Chem. Phys. 121, 7347 (2004).
[33] W. Kob and H. C. Andersen, Phys. Rev. Lett. 73, 1376 (1994); Phys. Rev. E 51, 4626 (1995); Phys. Rev. E 52, 4134 (1995).
[34] A. Attili, P. Gallo and M. Rovere in preparation.