Mode coupling behavior of a Lennard Jones binary mixture: a comparison between bulk and confined phases

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We present a quantitative comparison at equivalent thermodynamical conditions of bulk and confined dynamical properties of a Lennard Jones binary mixture upon supercooling. Both systems had been previously found to display a behavior in agreement with the Mode Coupling theory of the evolution of glassy dynamics. Differences and analogies of behavior are discussed focusing in particular on the role of hopping in reducing spatially correlated dynamics in the confined system with respect to the bulk.

I. INTRODUCTION

The structural and dynamical properties of bulk supercooled liquids are now relatively well understood in the range close to the crossover temperature of the Mode Coupling Theory of the evolution of glassy dynamics, MCT. This theory describes, in its ideal version, the relaxation mechanism of supercooled liquids as mastered by the cage effect. The motion of atoms or molecules is restricted by the presence of nearest neighbors that surround and trap the tagged particle forming a cage around it. When the cage relaxes, due to cooperative motion, the particle diffuses. Relaxation times of the cage diverge on approaching a temperature $T_C$ where, in this framework, the liquid undergoes a structural arrest. In most liquids this dynamical singularity is avoided since close to $T_C$ the hopping relaxation channel opens. The temperature of glass transition is reached when also hopping is frozen. In this context $T_C$ remains an important temperature that marks the ideal crossover from a regime mastered by the cage effect to one mastered by hopping effects. This crossover temperature can be estimated through an MCT analysis of dynamical properties of the liquid both with experiments and computer simulations.

Relaxation modes described by MCT are cooperative in character. Cooperativity is a basic concept in several theories and models of the glass transition. The existence of cooperative rearranging regions, CRR, intimately related to dynamic heterogeneities, can be a possible interpretative mechanism for the approach to the glass transition. The extent of the CRR is expected to increases with decreasing temperature. In the presence of a restricted environment the behavior of these regions might be modified and this might imply a change of the dynamical behavior. Confinement can therefore offer possible clues for a better understanding of general mechanisms for the glass transitions in the bulk.

To assess the validity and the possible limits of applicability of MCT in confinement can help to bridge the concepts of hopping, caging and dynamical heterogeneities. These phenomena appear in fact all fundamental ingredients for the glass transition to occur. Only very few computer simulation studies on the applicability of MCT on supercooled liquids in confined geometries are available. A detailed comparison of the dynamics of a glass former in the bulk and in a confined state can give new insights in understanding the behavior of the supercooled liquids. This comparison can nonetheless be quantitatively carried out only if it is performed at equivalent thermodynamical conditions.

In this paper we consider one of the most studied model for glass former liquids, a Lennard Jones binary mixture, LJBM, which is known to test MCT in its bulk phase. We carry on a direct comparison between a set of simulations that we have previously published of the LJBM confined in a disordered array of soft spheres and an equivalent bulk phase. The LJBM hosted by the matrix is in a strong confining environment where a large fraction of particles are interface. This microporous medium can be considered a model for real compounds like silica xerogels. The confined liquid has been found in our previous works to test MCT. Recently the mean square displacement results for this system have also been found to fit in the framework of a recently proposed mean field theory of the glass transition.

A difficulty to face in the comparison with the bulk is the presence of variations of the local density of the confined LJBM as a function of temperature due to the soft sphere repulsive potential. There is not a unique way to define a free volume. Therefore, in order to obtain a quantitative comparison of the dynamical properties we performed here computer simulations of the bulk liquid along a thermodynamical path where the $(T, P)$ values follow the isochore obtained for the confined system upon supercooling. This implies that for the bulk phase analyzed in this paper the approach to $T_C$ is not obtained along isochoric, isobaric or isothermal paths, as usually done for bulk glass formers.

The paper is structured as follows: in the next section
we present the details of the newly performed bulk simulations, and a brief description of the previously studied confined LJBM. The third section describes the behavior of the density correlators in the $\alpha$ relaxation region. The fourth section explores the role of hopping in bulk compared to confinement. The fifth section presents an analysis of dynamical clusters in the two systems. Last section is devoted to conclusions.

II. SIMULATION DETAILS

We report data analysis obtained from molecular dynamics simulations trajectories of a Lennard-Jones 80:20 binary mixture (LJBM) defined as in ref. 2 in the bulk phase. The LJBM state points are simulated at the same temperatures and pressures of previously reported data from the same mixture in a confined phase.\textsuperscript{3,6,9}

In the following the 80% atoms will be referred to as A and the 20% as B.

In the confined system the LJBM was embedded in an off lattice matrix of soft spheres, labelled with S. The simulation box of the confined system contained a rigid disordered array of $N_S = 16$ soft spheres. A constant volume with a selected simulation box length $L = 12.6$ was used. For further details referring to the confined system see refs. 3,6,9.

Temperature and pressure of the bulk system during cooling and equilibration procedures were controlled via a Berendsen weak coupling to thermal and pressure baths. In this case a varying box length ranging from $L = 10.34$ to $L = 9.36$ upon decreasing temperature has been used.

For each thermodynamical point, molecular dynamics simulation to evaluate static and dynamical properties, have been then performed in the microcanonical ensemble for both bulk and confined systems.

The confined system was studied for temperatures ranging from $T = 5$ to $T = 0.37$, while the bulk range of temperature investigated for comparison goes from $T = 5$ to $T = 0.48$. $T = 0.37$ and $T = 0.48$ represent the lowest temperatures at which we are respectively able to equilibrate the confined and bulk system.

We used a timestep of 0.01 for $T > 0.53$ and 0.02 for $T < 0.53$ for the confined system and 0.01 for $T > 0.8$ and 0.02 for $T < 0.8$ for the bulk system. The total production time of the lowest temperature investigated, $T = 0.37$, was of $t_{\text{run}} = 14$ millions of timesteps. These values would correspond for liquid Argon to $T = 44.3 \, K$ and $t_{\text{run}} = 4.2 \, \mu s$.

The behavior of total energy, pressure and, for the bulk, density as a function of temperature is depicted in Fig. 1. Thermodynamic ($T, P$) points of the bulk follow the isochoric path found upon supercooling for the confined system.\textsuperscript{4} In the same panel we note also that upon supercooling, in the range of investigated temperatures, an increase of number density $\rho$ occurs in the bulk system where $\rho = 0.9 \pm 1.2$. In the confined system the density cannot be exactly calculated due to the presence of the repulsive soft sphere potential. However a qualitative estimate of the density of the confined mixture carried out with Voronoi tessellation has been reported in ref. 3. The range of densities estimated with this method for the confined system was found to be $\rho = 0.7 \div 1.2$, similar to that found in our equivalent bulk liquid.

In the lower panel of Fig. 1 we also reported the values of the total equilibrium energies per atom of the two systems. A similar trend is observed. As expected the energy of the confined system is shifted above the bulk one due to the additional term of interaction with the soft spheres in the potential energy. At higher temperatures an average increase of about 5 $\epsilon_A$ of the internal energy of the confined system is found. This difference tends to reduce asymptotically to 3.0 $\epsilon_A$ upon cooling. Over the range of temperatures and densities investigated the bulk and the confined liquids show no signatures of phase separation as we can deduce from the smoothness of the curves. This is consistent with a study of the liquid limits of the bulk LJBM.\textsuperscript{15}

We found that the main features of the pair correlation

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig1.png}
\caption{a) Pressure as a function of inverse temperature of both bulk and confined systems; the corresponding bulk density is also shown. b) Total energy per atom versus inverse temperature for bulk and confined systems. In both panels, lines depict simple polynomial interpolations.}
\end{figure}
functions and of the static structure factors of our bulk LJBM (not reported) are similar to those of the confined liquid.

III. THE ALPHA-RELAXATION REGION

The slowing down of the dynamics of a supercooled liquid on approaching $T_C$ can be characterized by analyzing the temperature dependence of the single particle or self intermediate scattering function $F^{(s)}(Q,t)$, SISF, for both types of particles. In this section we report the bulk results on the SISF analysis compared to the previously obtained results for the confined system.

The temperature dependence of the bulk SISF is analyzed in the following for wave lengths corresponding to the inter-particle spacing, i.e. for $Q = Q_{\text{MAX}}(T)$, located at the first peak of the static structure factors. Around these values of $Q$ MCT features are best evident. Since the positions of the diffraction peak show a weak $T$-dependence in order to pursue consistently our comparison we use for the bulk analysis the same values of $Q_{\text{MAX},A} = 7.06$ and $Q_{\text{MAX},B} = 5.90$ that we used in the confined LJBM.

The results for $A$ particles are reported in Fig. 2 for both bulk and confined systems on the same scale for a close comparison. Similar results are found for $B$ particles (not reported). From the figure we recognize upon supercooling for both bulk and confined mixtures the onset of the MCT predicted two-step relaxation scenario. At $T_C$ in the idealized version of MCT this scenario leads to the bifurcation of the long time limit of the correlator. This limit also called non ergodicity parameter, is zero for the liquid and jumps to a finite value on crossing the MCT critical line. The existence of the plateau is related to the MCT two time fractals. The dynamical regime that covers the approach to the plateau of the correlator is referred in literature as the $\beta$-relaxation regime. This regime is followed by the $\alpha$-relaxation that starts when the correlator departs from the plateau. For long times, in the late $\alpha$-relaxation regime, the intermediate scattering function decays to zero in a non-exponential fashion.

We note that the shape of the correlators in bulk and confined liquids differs. In particular at the lowest temperatures investigated, $T = 0.48$ and $T = 0.37$ respectively for bulk and confined systems, the extension of the plateau rapidly grows spanning up to over three decades in the bulk, while it is much less defined and covers only one decade in the confined system. After the plateau the correlator decays much faster to zero in the bulk than in the confined.

FIG. 2: Self part of the intermediate scattering function for the $A$ particles, $F^{(s)}(Q_{\text{MAX}}, t)$, for different temperatures for the bulk (a) and the confined (b) systems. The correlators are evaluated at $Q_{\text{MAX}} = 7.06$, the position of the first peak in the static structure factor for the $A - A$ correlation. The dashed lines are fits to KWW stretched exponential (see Eq. 1), in the region of the late $\alpha$-relaxation.

FIG. 3: Fitting parameters of the KWW curves plotted in Fig. 2 for both bulk and confined systems as functions of the temperature. Circles refer to bulk $A$ (filled) and $B$ (open) particles. Squares refer to confined $A$ (filled) and $B$ (open) particles. a) Relaxation times $\tau_A(T)$ and $\tau_B(T)$. b) Stretching parameter $\beta_A(T)$ and $\beta_B(T)$. c) Form factor $f_{QA}(T)$ and $f_{QB}(T)$. 

\[f_{QA}(T) = \frac{\tau_A(T)}{\tau_B(T)}\]
in the confined system where long time tails related to a more consistent stretching of the relaxation law can be observed.

The $T$–dependence of the $\alpha$–relaxation time $\tau_\alpha(T)$, can be extracted from the fits of the $F^{\alpha}(Q,t)$ to the Kohlrausch-Williams-Watts (KWW) stretched exponential function

$$\phi_\alpha(t) = f_Q(T) \exp \left[-(t/\tau_\alpha(T))^{\beta(T)}\right],$$

where $\beta(T)$ is the stretching parameter. $f_Q(T)$ can be considered as an effective Lamb Mössbauer factor and is related to the height of the plateau. In the ideal version of the theory this height coincides with the non ergodicity parameter for $T \leq T_C$, $f_Q(T) = \lim_{t \to \infty} \phi_\alpha(t)$.

Although the KWW functional form is not an exact solution of MCT equations, it has been shown that it is able to reproduce remarkably well the behavior of the numerical solution evaluated from these equation, in the $\alpha$–relaxation regime.

![FIG. 4: Power law fits of the diffusion coefficients (a) and of the inverse relaxation times (b) as a function of temperature for confined (squares) and bulk (circles) liquids. In (c), only for the bulk case, analogue power law behavior of $D$ (triangles) and $\tau$ (diamonds) as functions of density is shown. In all panels filled symbols refer to A particles, open symbols to B particles. The extrapolated MCT parameter, $T_C$ and $\rho_C$, and exponent $\gamma$, are reported in Tab. I.](image)

The results of the fit are reported, together with the density correlators, in Fig. 2 where we can see that the agreement of the fitting function to the correlators curves is very good.

Fitting parameters for both particle types in bulk and confined systems as functions of the temperature, are shown in Fig. 3.

As expected for systems testing MCT, the relaxation times $\tau_A(T)$ and $\tau_B(T)$ increase dramatically as the temperature is lowered, varying up to four order of magnitude in the $T$–ranges investigated. Similar trends in bulk and in confinement are observed but we note that the relaxation times for the confined system are consistently smaller than those of the bulk. This is a clear indication of a faster dynamics due to repulsive confinement.

The departure from the Debye exponential relaxation is quantified by the stretching parameters $\beta_A$ and $\beta_B$. These can be connected to the presence of heterogeneity in the dynamics, due to the coexistence of dynamical regimes characterized by a distribution of relaxation times. The stretching parameters of both systems have values close to 1 (simple Debye relaxation) at high temperatures. MCT asymptotically predicts these parameters to have a weak temperature dependence. This prediction is satisfied in the bulk liquid, where, upon decreasing the temperature, the parameter is seen to lower and to reach a constant plateau value close to 0.8, whereas, in the case of the confined system, the parameter does not reach a constant value, but instead keeps on decreasing regularly down to 0.4 at the lowest temperature investigated. We will see in the next section that the latter behavior can be related to the presence of significant hopping processes found in the confined system at these temperatures.

The $T$–dependence of the parameter $f_Q$ (height of the plateau) is rather weak as predicted by MCT and has a similar trend in both confined and bulk systems. We found $0.70 \leq f_Q \leq 0.77$ for the bulk with similar values

| TABLE I: Power-laws fit parameters of bulk and confined mixtures, for A and B atoms. In the upper half of the table are reported values obtained from the analysis of diffusion constants $D$, while in the lower part values obtained from the analysis of relaxation times $\tau_\alpha$. |
|-----------------|-------|--------|--------|-------|
|                | $A$   | $B$   | $A$   | $B$   |
| $(from \ D)$   | 1.12  | 1.12  | 0.36   | 0.36  |
| $\rho_C$       | 2.09  | 2.09  | 1.82   | 1.82  |
| $\gamma$       | 2.00  | 2.00  | 2.00   | 2.00  |

![TABLE I: Power-laws fit parameters of bulk and confined mixtures, for A and B atoms. In the upper half of the table are reported values obtained from the analysis of diffusion constants $D$, while in the lower part values obtained from the analysis of relaxation times $\tau_\alpha$.](image)
for different species. For the confined system different values for $A$ and $B$ particles were found: $0.66 \leq f_Q \leq 0.72$ for $A$ particles and $0.72 \leq f_q \leq 0.77$ for $B$ particles.

![Graph showing the intermediate scattering function for bulk and confined mixtures](image)

**FIG. 5:** Self part of the intermediate scattering function for the $A$ particles, $F_A^{(s)}(Q_{\text{MAX}}, t)$, with $Q_{\text{MAX}} = 7.06$, for different temperatures, scaled by $\tau_\alpha$ (obtained from a KWW fit, see Fig. 3); the dashed curve is the fit to a von Schweidler law defined in Eq. 4, (see Tab. II). In (a) are presented bulk correlators at temperatures $0.48 \leq T \leq 0.8$, in (b) confined correlators at temperatures $0.37 \leq T \leq 0.43, 0.8$.

**TABLE II:** Von Schweidler fit parameters of bulk and confined mixtures, for $A$ and $B$ atoms.

| Bulk Mixture | Conf. Mixture |
|--------------|---------------|
| $f_Q$        | $A$           | $0.81$ | $0.81$ |
| $f_q$        | $B$           | $0.52$ | $0.53$ |
| $h_Q$        | $A$           | $0.460$ | $0.531$ |
| $h_q$        | $B$           | $0.216$ | $0.355$ |
| $b$          | $A$           | $0.197$ | $0.216$ |
| $t_\alpha^{2}$ | $B$          | $0.179$ | $0.220$ |

According to the ideal version of MCT, the relaxation times, $\tau_\alpha$, as well as the diffusion coefficients, $D$, are expected to follow asymptotically a power-law divergence as functions of temperature and density near the cross-over point $(T_C, \rho_C)$

$$D, \tau_\alpha^{-1} \propto (T - T_C)^\gamma, \quad D, \tau_\alpha^{-1} \propto (\rho_C - \rho)^\gamma,$$  

where $T_C$ and $\rho_C$ are respectively the cross-over temperature and density of the theory, and $\gamma$ is the exponent parameter. The fits to power-laws are reported in Fig. 5 overlaid to $\tau_\alpha$ and $D$ data found in both confined and bulk systems. The coefficients $D$ are extracted from the mean square displacements (MSD), not reported, in the diffusive regime.

We found good agreement of the relations of Eq. 2 with the data in the range $0.48 \leq T \leq 0.80$ $(1.16 \leq \rho \leq 1.22)$ for the bulk to be compared to $0.41 \leq T \leq 0.58$ obtained for the confined system. These values correspond, in terms of the small parameter of the theory $\epsilon = \left( \frac{T_C - T}{T_C} \right)$, to a relative reduction of the ideal MCT range of applicability in confinement of about 30% with respect to the bulk.

Results for the fitting parameters are reported in table IV $T_C, \gamma$ and (for the bulk only) $\rho_C$, are similar for the different species $A$ and $B$ as predicted by the theory. The same crossover temperature is found from $D$ and $\tau$. In the confined liquid $T_C \approx 0.36$ is sensibly lower than in the bulk $T_C \approx 0.45$.

The critical density of the bulk is slightly higher than the density simulated for the lowest temperature bulk, and also very close to the estimate of the density of the lowest temperature in the confined system, see Sec. II.

We note that the values of $\gamma$ extracted from $\tau_\alpha$ are similar for both bulk and confined mixtures, $\gamma \approx 2.8$. Contrary to the MCT predictions, the values of $\gamma$ extracted from $D$ differ from those extracted from $\tau_\alpha$ both in bulk and in confined systems. This difference is more marked in the presence of confinement and a possible source of these discrepancies is the presence of hopping that will be discussed in sec. IV.

The time-temperature superposition principle, TTSP, predicted by MCT to hold asymptotically near $T_C$, states that the shape of the correlator curves in the late $\beta$-relaxation and early $\alpha$-relaxation time regimes does not depend on temperature. Consequently the intermediate scattering functions can be written as

$$F^{(s)}(Q, t) = \hat{\phi}_Q(t/\tau_\alpha(T))$$  

where $\tau_\alpha$ is a time scale associated to the $\alpha$-relaxation decay of the correlation function and $\hat{\phi}_Q$ is a master function. We used in the scaling of the SISF of $\tau_\alpha(T)$ obtained via KWW fits.

The correlators are plotted for different temperatures versus rescaled time $t/\tau_\alpha(T)$ in Fig. 5 for $A$ particles. The intermediate scattering functions reported in the figure are evaluated in the same temperature ranges used in the analysis of power-law divergence, i.e. $\epsilon \sim 0.4$ for the confined mixture and $\epsilon \sim 0.7$ for the bulk one. From the figures it is seen that also for the bulk with varying density the rescaled correlator curves fall on top of each other within the the late $\beta-$relaxation region up to the $\alpha-$relaxation time range. Similar results hold also for $B$ particles (not shown).

MCT theory predicts also a precise functional form of the master function $\hat{\phi}(t)$ in the $\beta-$relaxation regime. The
form is a von Schweidler (VS) power law,

$$\dot{\phi}(t) = f_Q^c - h_Q(t/\tau_a)^b.$$  \hspace{1cm} (4)

Best fits to our master plots are included in Fig. 5 (dashed lines). Rescaled time intervals used in the fits are $10^{-3} \leq t/\tau_a \leq 10^0$. The values of the free parameters, $f_Q^c$, $h_Q$ and $b$ are reported in Tab. II. As it can be seen from the figures, there is a good agreement with the data while we observe that the prediction of MCT that $b$ should be the same for both A and B particles is verified only in confinement. The better agreement with MCT of the confined system might be related to packing constraint induced by the confined geometry and the repulsive potential that further reduce the tendency of the mixture to phase separation. As already observed for the stretching parameter the von Schweidler exponent $b$ lowers in confinement reflecting a larger distribution of the relaxation times. The critical non ergodicity parameter $f_Q^c$ offers an estimate of the mean square displacement $r^2$ of the particles at a time $t = 1/\omega_c$, where $\omega_c$ is the cutoff frequency below which the whole alpha peak is located, i.e. the time where the $\alpha$ relaxation starts. In fact:

$$\ln f_Q^c = \frac{-(r_s Q)^2}{3} + O(Q^4)$$ \hspace{1cm} (5)

The values of $r_s$ extracted both from Eq. 5 are consistent with the ones obtained from the plateau of the MSD (not shown) as reported in Tab. II. We observe that A and B particles in confinement and B particle in bulk move on similar distances while the packing of large A particles is stronger in the bulk.

We note that the VS law has been tested to be valid for an extended range of $Q$ around the peak of the structure factor for both confined and bulk systems, not shown here.

**IV. HOPPING EFFECTS**

**A. van Hove Correlation Function**

To investigate the relevance of hopping effects above $T_c$ in our systems we now investigate the distribution of the average distances. This can be done by means of the self part of the van Hove correlation function (VHCF) defined as

$$G^{(s)}(r, t) = \frac{1}{N} \sum_{\nu=1}^{N} \langle \delta(r_{\nu}(t) - r_{\nu}(0) - r) \rangle,$$ \hspace{1cm} (6)

This function is related to the intermediate scattering function via Fourier transform and $4\pi r^2 G^{(s)}_\mu(r, t)$ is the probability density for a particle of specie $\mu$ of being displaced of a distance $r$ in a time interval $t$.

The van Hove correlator as a function of the distance $r$, has been evaluated for different temperatures and for several different times, that span from the ballistic to the diffusive regime of the MSD, $10^{-2} \leq t \leq 10^0$, with a $t \sim 2^n$ geometric progression. The evaluations have been carried out for both A and B particles and for each system.

In Fig. 6 we report a comparison between the distance distributions found in the confined and bulk LJBM (panel (a) and (b)) respectively. In these plots both systems are observed at the same temperature $T = 0.48$, i.e. the lowest temperature simulated for the bulk liquid. From these figures we can see that in both systems the distribution shows a simple Gaussian shape. The Gaussian peak maxima shift at greater distances, when the positions of the peaks in the van Hove function (x axis), for confined and bulk systems respectively, versus times (y axis).
cluster at the localization radius \( r \sim 0.15 \). At the same temperature, for the confined system we found a similar but less pronounced clustering in the more limited range \( 3 < t < 2 \times 10^2 \) and at \( r \sim 0.2 \). The position of the peak of the VHCF remains constant for the presence of oscillating particles which are trapped in their transient cages. The time ranges in which we observe this trapped dynamics correspond to those of the plateau seen in the SISF. In panels (c) and (d) we observe, in a double logarithmic scale, the positions of the peaks in the van Hove function (x axis), for confined and bulk system respectively, versus times (y axis).

In the study of the supercooled phase in the asymptotic region near \( T_C \) of MCT, a more significant comparison for the details of the dynamical behavior is achieved by considering not absolute temperatures, but instead temperatures relative to the critical temperature, i.e. thermodynamic conditions with the same value of the small parameter of the theory \( \epsilon \). This comparison is supported by the validity of the TTSP for the supercooled regime. In the previous section we demonstrated that this principle is indeed satisfied by our systems.

We now compare in Fig. 7, in the same fashion, the VHCF for the two lowest temperatures simulated in bulk and confinement. These temperatures correspond to the same distance from the respective \( T_C \). Their value of the small parameter is \( \epsilon = 0.04 \). An interesting feature is observed for the confined case. The particles remain trapped in the frozen cage for a time longer than the bulk. Escape is guaranteed only by hopping. In this correlator in fact now three hopping peaks are clearly visible for the A particles while hopping is totally absent for this kind of particles in the bulk for the time scales of the figure.

In order to evidence the behavior of the \( G^x(r,t) \) at higher times (and higher distances) we show in Figs. 8 a four-panel comparison of the correlators reported in a linear scale, between correlation functions for A and B atoms, bulk and confined systems. In Fig. 8 the comparison is reported only for A particles in bulk and confinement at a high temperature and a low temperature. While at high temperature the systems exhibit very similar correlators at the same times, larger differences are found at the lower temperature, where the behavior of the van Hove correlators indicates a much greater mobility and a more evident presence of hopping of particles in the confined system than in the bulk. In Fig. 8 the comparison is carried out at the same low temperature, \( T = 0.48 \), for both kind of particles. From the figure it can be argued that the small B particles have a larger tendency to exhibit hopping in the bulk. It is also clear that confinement succeeds in reducing hopping...
for $B$ particles and to enhance hopping for $A$ particles. The comparison carried out at the same $\epsilon$ is reported in Fig. 10. From this comparison it is even more clear than in the former figures what is the fundamental difference between the dynamics in the bulk and the dynamics in confinement. In the bulk we have hopping only for $B$ particles. For these particles the phenomenon is marked, but in a quite distinct time range with respect to the time range of the caging. In confinement for both $A$ and $B$ particles we have a marked hopping already when a part of the particles is still rattling in the cage. The overall result is that dynamics appears similar for $A$ and $B$ particles only in confinement.

B. Non-Gaussian Parameter

The deviation from the Gaussian behavior of $G^{(s)}_\mu (r,t)$ can be analyzed in terms of the non-Gaussian parameter,

$$\alpha^{(2)} = \frac{\langle r^4(t) \rangle - \langle r^4(t) \rangle_{\text{Gauss}}}{\langle r^4(t) \rangle_{\text{Gauss}}} = \frac{3 \langle r^4(t) \rangle}{5 \langle r^2(t) \rangle^2} - 1$$

which is the relative deviation between the $\langle r^4(t) \rangle$ obtained from simulations and the value it should have if $G^{(s)}(r,t)$ was Gaussian. The non Gaussian parameter can be studied in order to quantify the effects of dynamic heterogeneity, as hopping processes, and it can also be obtained experimentally from the Q-dependence of the Debye Waller factor.

In figure 11 $\alpha^{(2)}(t)$ is shown as a function of $t$ for $A$ and $B$ particles for different temperatures. The same result for the confined system is reported for comparison. We note that the $\alpha^{(2)}(t)$ behavior for both systems is similar to that found in several other simulations on bulk liquids close to glass transition: $\alpha^{(2)}(t)$ increases significantly in the late $\beta$ relaxation regime, near the onset of the $\alpha$ relaxation, where it reaches its maximum, then it decays to zero as $t \to \infty$. Furthermore, a master curve is found overlapping the individual curves in a time interval just before they attain their maximum. However we note that, in our confined system, such master curve is considerably less defined than in the bulk.

In the bulk system the non Gaussian parameter appears very different for $A$ and $B$ particles and never exceeds the value of 2 for $A$ particles. This can be connected to the observed negligible hopping above $T_C$ for $A$ particles. In the confined system we have instead similar parameters for $A$ and $B$ particles and their values grow

![Fig. 9: Comparison between bulk and confined systems and between different species of particles, for the self part of the van Hove correlation function $G^{(s)}(r,t)$. The correlators are evaluated at the same temperature, $T = 0.48$, and for different times, some of these evidenced with thicker lines. The four panels, adopting the same scales, represent $G^{(s)}(r,t)$ for: a) bulk system, $A$ particles; b) bulk system, $B$ particles; c) confined system, $A$ particles; d) confined system, $B$ particles.](image1)

![Fig. 10: Comparison between bulk and confined systems and between different species of particles, for the self part of the van Hove correlation function $G^{(s)}(r,t)$. The correlators are evaluated at the same value of the small parameter $\epsilon = 0.04$ of MCT, which correspond to temperatures $T = 0.48$ for the bulk liquid and $T = 0.37$ for the confined system. The correlator is shown in the time space region where hopping is visible, i.e. the late $\beta$–relaxation regime. The functions are normalized to unity. The four panels, adopting the same scales, represent $G^{(s)}(r,t)$ for: a) confined system, $A$ particles; b) bulk system, $A$ particles; c) confined system, $B$ particles; d) bulk system, $B$ particles.](image2)
FIG. 11: The non-Gaussian parameter $\alpha_1^{(2)}(t)$ (continuous lines) and $\alpha_2^{(2)}(t)$ (dashed lines) for the bulk (a) and confined (b) systems. Higher curves correspond to lower temperatures $0.48 \leq T \leq 5.0$ for the bulk and $0.37 \leq T \leq 5.0$ for the confined systems. Thicker lines in both figures are associated to the lowest temperature ($T = 0.48$) for the bulk.

FIG. 12: Distribution of the size $N_p$ (number of particles) of the dynamical clusters found in the confined (first row of panels) and in the bulk (second row of panels) liquids, for the temperatures $T = 0.58$, $0.48$ and $0.37$. Different curves correspond to different time ranges used in the sampling (lifetime of the clusters).

substantially as we supercool. For the lowest temperature investigated in confinement the peak heights are around 5. Hopping appears therefore to cause a much more marked deviation from gaussianity than MCT behavior and it also seems to lead to a disappearance of the master curve.

V. CLUSTER DYNAMICS

Extensive investigations of LJBM with a large number of particles have shown recently the important role of the cooperative molecular motion in the interpretation of the slow dynamics and the behavior of the relaxation in liquids upon supercooling close to $T_C$. We expect that confinement induces modifications in the CRR mechanism. We have investigated for our LJBM both in bulk and in confined phases the possible existence of a spatially correlated dynamics. An estimate of the typical distance of the particles correlation can be obtained from an analysis of clusters of nearest neighbors. In our analysis two particles belong to the same cluster if the maximum distance they reach from each other within a fixed time $\Delta t$ is less equal than $\sigma_{\mu\nu} + \Delta \sigma$ where $\Delta \sigma = 0.1$. In Fig. 12 we show the distribution functions of the size of the number of particles, $N_p$, of the dynamical clusters for different time ranges $\Delta t$ used in the sampling at different temperatures.

We observe that in the bulk the larger clusters, corresponding to the shorter fixed times, arrive to circa 32 particles and that at the lowest temperature investigated the distribution function of the clusters remains unchanged up to $\Delta t = 5$. In confinement the maximum size of the clusters does not exceed 16 particles and persists only for a very short time also for the lowest temperature. In the bulk a very precise analysis of these spatial correlations has been already carried out for the same LJBM. The authors use a much larger sample and are able to distinguish between mobile and immobile particles. Both these kind of particles show a distribution of the sizes similar to what found in our smaller bulk sample. Comparing our analysis of the bulk and confined systems we observe that in confinement spatial correlations are strongly depressed. This can be connected to the fact that at variance with the bulk in the confined system hopping mechanisms intervene while cages are still re-
laxing. The authors of ref.2 in their study of the bulk phase of the LJBM underline in fact the importance of subsequential relaxation processes for spatially correlated dynamics. At any given time most particles are localized in cages and a small fraction forms cooperative strings. Once rearranged these particles become caged and others become mobile. The clarification of this point needs further investigation and can be possibly connected with the behavior of the inherent structures in confinement.18

VI. CONCLUSIONS

We performed an accurate study of the behavior of a LJBM upon supercooling. The system has been studied along the thermodynamical path corresponding to the isochoric path of a previous study of the same liquid in confinement. In this way we could carry out a quantitative comparison between the two systems.

The analysis of the density correlators in the alpha-relaxation region shows that the MCT predictions are satisfied by our bulk system that approaches the critical curve upon decreasing temperature with a path where the volume is not constant.

On comparing the SISF of the bulk with the confined one we have confirmed and quantified the differences and analogies between the two systems that we did hypothesize in our previous studies.8,9,10 In particular we have observed a difference in the slope of the tail of the correlators and a much less defined plateau in confinement. This leads to a substantially lower value of the stretching parameter $\beta$. Besides the $\beta$ values do not reach a constant value upon decreasing temperature at variance with those of the bulk liquid. The crossover temperature in the confined case is lower with respect to bulk.

Discrepancies with the MCT predictions for the exponent $\gamma$ determining the asymptotic behavior of the relaxation time and the diffusion coefficient are found to be more marked in confinement. This can be ascribed to the hopping phenomenon that in confinement plays above and near $T_C$ a more significant role than in the bulk. In the bulk in fact hopping effects appear only for the smaller $B$ particles and in a time range well distinct from the time range of the cage effect. In confinement we observe hopping effects for both species of particles in a time scale that coincides with the time scale of caging. As a consequence MCT behavior is partially hidden. In fact the TTSP is verified also in confinement but in a much smaller range of temperatures, analogously to the power law behavior. Also the prediction that the exponent $b$ extracted from the von Schweidler should be the same for $A$ and $B$ particles is verified only in confinement.

Hopping effects determine deviation from gaussianity more marked in confinement than in bulk. The non Gaussian parameters are different for $A$ and $B$ particles in the bulk but they are very similar in confinement.

Finally our comparison of the cluster dynamics in confinement and in bulk shows that clusters in the confined system have smaller sizes and last shorter time than in the bulk. Further analysis of cooperativity in confined glass former would require to study larger systems, but present results show that in the presence of a restricted environment cooperativity is at least partially inhibited.

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