Lennard-Jones binary mixture in disordered matrices: exploring the mode coupling scenario at increasing confinement

2011 J. Phys.: Condens. Matter 23 234118

(http://iopscience.iop.org/0953-8984/23/23/234118)

IOP Publishing Journal of Physics: Condensed Matter

J. Phys.: Condens. Matter **23** (2011) 234118 (7pp) doi:10.1088/0953-8984/23/23/234118

Lennard-Jones binary mixture in disordered matrices: exploring the mode coupling scenario at increasing confinement

P Gallo[1] **and M Rovere**[1,2]

[1] Dipartimento di Fisica, Università Roma Tre, Via della Vasca Navale 84, I-00146 Roma, Italy
[2] CECAM-EPFL, Lausanne, Switzerland

E-mail: gallop@fis.uniroma3.it

Received 20 October 2010, in final form 5 January 2011
Published 25 May 2011
Online at stacks.iop.org/JPhysCM/23/234118

Abstract

We present results of molecular dynamics simulations performed on a Lennard-Jones liquid binary mixture confined in matrices of soft spheres at increasing packing fraction. We study the dynamical properties of the liquid at a given density upon supercooling. Our aim is to test the validity of the mode coupling theory in predicting the behaviour of the glass forming liquid when it is under confinement in a disordered matrix. We use two different methods to build up the confining environment. We focus in particular on the behaviour of the single particle density correlators. We find a close agreement with the mode coupling theory at least for all the range of packing fractions examined. Discrepancies between the theory and the computer simulation results can be attributed to hopping effects which are more important at increasing confinement.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

The dynamical behaviour and the glass transition of supercooled liquids are expected to be modified in confinement. This issue has attracted great attention in the last fifteen years due to the connection with problems in biology, geophysics and various technological applications [1–4].

In glass forming liquids the glass transition phenomena persist in confinement, but experiments and computer simulations find that the behaviour upon supercooling depends on the geometry and the type of substrate. Generally speaking, so far the role of the restricted geometry [5] and the decrease of the free volume accessible to the liquid in the approach to the glass transition are not completely understood. From a fundamental point of view an important achievement has been that the mode coupling theory (MCT) [6–8], which is able to predict the evolution of the glassy dynamics for many glass forming systems, keeps its validity also in various types of confinement [9–18]. This is particularly relevant since MCT is able to give a unified description of the phenomena taking place upon supercooling in spite of the differences in the details of the systems investigated.

In this framework liquids confined in disordered porous matrices like silica xerogels are of particular interest. From the theoretical point of view they can be modelled by confining the liquid in a system of quenched–annealed (QA) spheres, a model introduced in the past to study the change in the phase diagram induced by disorder [19–21]. For these models a theoretical approach has been developed very recently [22–25] which combines the replica Ornstein–Zernike (ROZ) method applied to liquids embedded in QA matrices (ROZ) [20, 26, 27] with the MCT. Computer simulations of hard or soft spheres in QA matrices confirmed the predictions of the ROZ–MCT [28]. In these, as in other studies [29], new scenarios appear characterized by higher order MCT transitions [30, 31] as found in studies of colloidal systems [32–34].

The Lennard-Jones binary mixture (LJBM), as defined by Kob and Andersen [35–37], has been considered since its introduction as a prototype of a realistic glass forming system. It has been shown that its dynamical behaviour upon supercooling is in strict agreement with the MCT predictions.

In previous studies of the LJBM confined in a random matrix of soft spheres [11–14] we showed that the main

features of the agreement with MCT are maintained in confinement. We found that the MCT was able to describe the dynamical behaviour of the confined LJBM with a decrease of the crossover temperature T_C with respect to the bulk. A reduction of the range of validity of the MCT is found, however, upon increasing the size of the soft spheres [38], a signature that the relevance of hopping effects increases as the disposable volume for liquid decreases. It is worthwhile to explore in more detail the volume excluded effects on the MCT behaviour, for this reason in this paper we consider the LJBM confined in a random matrix of soft spheres and test the MCT behaviour at very high packing fraction of the soft spheres. We also compare two different methodologies able to realize QA matrices.

In section 2 we briefly introduce the predictions of the MCT which are relevant for the interpretation of the results of the present study. In section 3 we explain the model and the methods we adopted in our computer simulations. We report and discuss the results obtained for the lower packing fractions in section 4 and for the highest packing fractions in section 5. Section 6 is devoted to conclusions.

2. Mode coupling relaxation scenario

We refer here to the simplest version of the mode coupling theory of the evolution of glassy dynamics [6–8]. MCT in its idealized version predicts that below the melting temperature an undercooled liquid undergoes a transition from an ergodic behaviour to a no longer ergodic behaviour at a crossover temperature T_C. The predictions of the theory are valid in the asymptotic regime very close to T_C. In particular here we consider the density–density correlation functions, but the predictions of MCT are formulated for any dynamical variable with an overlap with the fluctuations of the density.

The MCT description of the dynamical behaviour of a supercooled liquid is based on the idea that above T_C the particle is trapped in the cage of its nearest neighbours (cage effect). After a certain time the cage relaxes and the Brownian diffusion regime is restored. So the dynamical behaviour is characterized by a two step relaxation. In this paper we report calculations of the self-intermediate scattering function (SISF) $F_S(Q \cdot t)$, the Fourier transform of the self-density correlation function, and the mean square displacement (MSD) $\langle r^2(t)\rangle$. For the SISF reported as a function of time MCT predicts that after an initial fast decay corresponding to the ballistic regime the function shows a plateau related to the cage effect. After the plateau the SISF decays at long time with a stretched exponential (α-relaxation) and it is well approximated by the Kohlrausch–Williams–Watts (KWW) function

$$F_S(Q, t \to \infty) \approx f_Q(T) \exp[-(t/\tau)^\beta] \tag{1}$$

where $f_Q(T)$ is the Lamb–Mössbauer factor and is related to the height of the plateau, β is the Kohlrausch exponent with the condition $0 < \beta < 1$ and τ is the relaxation time. MCT predicts that as T decreases and approaches T_C the relaxation time diverges with a power law

$$\tau = C(q)(T - T_C)^{-\gamma} \tag{2}$$

Table 1. Interaction parameters between A and B (Lennard-Jones potential) particles in LJ units.

Atom pair	ϵ	σ
A–A	1.0	1.0
B–B	0.88	0.5
A–B	0.80	1.5

where the exponent γ must be $\gamma > 1.766$.

Also the behaviour of the MSD of a supercooled liquid is determined by the cage effect. After the ballistic regime the MSD shows a plateau related to the rattling of the particle in the cage. After the plateau the Brownian regime is recovered and the diffusion coefficient D can be extracted according to the Einstein relation $\langle r^2(t)\rangle = 6Dt$. Since $D \propto \tau^{-1}$ MCT predicts that

$$D \propto (T - T_C)^\gamma. \tag{3}$$

This scenario is predicted by the simplest version of the MCT. In this framework the theory neglects completely the hopping effects. In real liquids the dynamical singularities are avoided since close to T_C hopping effects restore ergodicity. Nevertheless the agreement with MCT can be tested by extrapolating to the asymptotic limit the different dynamical quantities calculated or measured above T_C at decreasing temperature. Discrepancies between the MCT predictions and the computer simulation or experimental results can mainly be attributed to the presence of hopping. It is interesting to explore how relevant the hopping effects are in confinement in comparison with bulk.

We note moreover that hopping effects could induce a change of behaviour of τ (or D) at decreasing temperature. A crossover could take place from the MCT power law (2) at high $T > T_C$ to an exponential Arrhenius behaviour $\tau \sim \exp(A/T)$ at low T. So due to hopping the supercooled liquid could show a crossover transition from a fragile to a strong behaviour [39–42].

3. Models and methods

The liquid we consider in our molecular dynamics (MD) calculations is a binary mixture of particles A and B with composition 80% of particles A and 20% of particles B interacting with a Lennard-Jones (LJ) potential [35–37]

$$V_{\alpha\beta} = 4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12} - \left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right]. \tag{4}$$

The parameters are reported in table 1. In the following we will use the LJ units; length will be in units of σ_{AA}, energy in units of ϵ_{AA}, the temperature in units of ϵ_{AA}/k_B. The time is measured in units of $(m\sigma_{AA}^2/(48\epsilon_{AA}))^{1/2}$.

Our calculations were performed with 800 A particles and 200 B particles.

We add to the liquid a soft sphere system of particles m interacting with a potential

$$V_m = 4\epsilon_m\left(\frac{\sigma_m}{r}\right)^{12}. \tag{5}$$

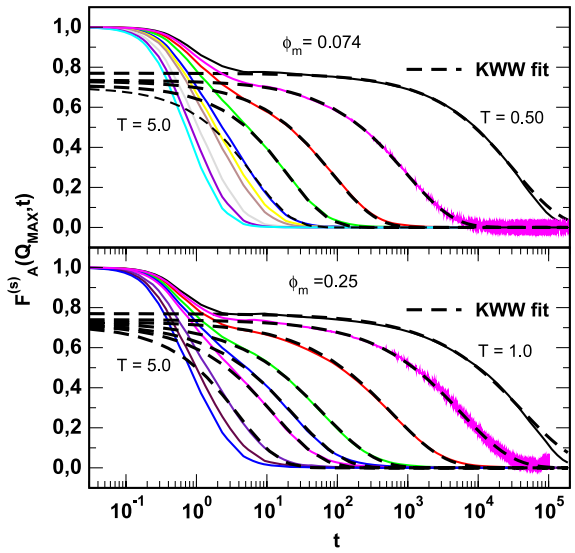

Figure 1. SISF of A particles as a function of time for different temperatures and packing fractions $\phi_m = 0.074$ (top frame), $\phi_m = 0.25$ (bottom frame). The broken lines represent the fits to the KWW law (see text). The time is in LJ units (see text).

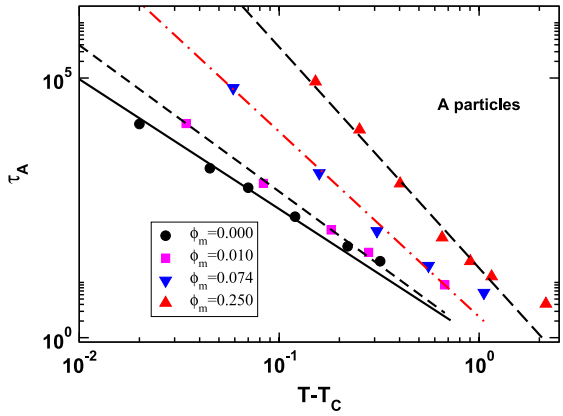

Figure 2. Relaxation time τ for A particles as a function of $T - T_C$ and for different ϕ_m. The broken lines are the fits to the power law (2).

We assume $\epsilon_m = 0.1$, while the size σ will be chosen as explained later. For the interactions between the liquid particles and the matrix spheres we assume the Lorenz–Berthelot rules:

$$\sigma_{m\alpha} = \tfrac{1}{2}(\sigma_m + \sigma_\alpha) \tag{6}$$

$$\epsilon_{m\alpha} = \sqrt{\epsilon_m \epsilon_\alpha}. \tag{7}$$

The confinement of the liquid can be realized with different methods. The important parameters in the confinement are the density of the liquid $\rho_f = (N_A + N_B)/V$ and the packing fraction of the spheres, given by

$$\phi_m = \frac{\pi}{6}\frac{N_m}{V}\sigma_m^3. \tag{8}$$

In the first calculations with packing fractions from $\phi_m = 0.01$ to 0.25 we used the so called inflation method. We added a number of A particles corresponding to the number of soft spheres we want to assume for the confining matrix $N'_A = N_A + N_m$. Then the system is equilibrated in a box with a volume which fixes the density of the liquid. After equilibration N_m of A particles randomly chosen are frozen and their potential is gradually switched to the soft spheres. This corresponds to an increase of the size of the N_m particles, a change in the repulsion and a switching off of the attraction. The procedure can be repeated to produce different realizations of the confining matrix, starting from the same equilibrated configuration.

Due to the difficulties encountered for higher packing fractions we used another method to build the starting configurations. It consists of equilibrating a three component system, where the third component is soft spheres with fixed diameter σ_m, while the value N_m is determined from the chosen ϕ_m. We will explain this procedure in more detail in section 5.

In all the cases the calculations of the dynamical quantities have been performed in the microcanonical ensemble after equilibration runs longer than the estimated relaxation time of the system.

4. Results from the inflation method

We studied the confined LJBM at a density of $\rho_f = 1.1$ and for temperatures in the range from $T = 5$ to 0.30. The sizes of the soft spheres were varied to obtain three packing fractions $\phi_m = 0.01$, 0.074 and 0.25. The case $\phi_m = 0.0$ corresponds to the bulk LJBM and is reported for comparison. The lowest temperature for which the system can be investigated increases with ϕ_m as $T = 0.30$ for the bulk ($\phi_m = 0.0$), $T = 0.35$ for $\phi_m = 0.01$, $T = 0.50$ for $\phi_m = 0.074$ and $T = 1.0$ for $\phi_m = 0.25$.

Upon supercooling for each system we calculated the mean square displacement (MSD) and the self-intermediate scattering function (SISF).

Examples of the SISF obtained in our simulations for the A particles are reported in figure 1, plotted for $Q = Q_{\max}$, the position of the highest peak of the structure factor, where the cage effect is best detected. Here the curves are shown for the two highest packing fractions $\phi_m = 0.074$ and 0.25. The onset of a plateau in the functions is seen to take place at decreasing temperatures. As explained above this plateau is the signature of the onset of the cage effect. Approaching the lowest temperatures, $T = 0.5$ for $\phi_m = 0.074$ and $T = 1.0$ for $\phi_m = 0.25$, the two step relaxation phenomenon predicted by the MCT is evident. After the plateau the α-decay at long time can be fitted with the KWW equation (1) and the parameters for A and B particles can be obtained.

In particular, from the complete analysis of the SISF it is possible to extract the α-relaxation time τ as a function of the temperature for the different cases. For each ϕ_m the power law (2) predicted by MCT is found as an asymptotic limit in approaching the ideal crossover temperature T_C.

In figure 2 we show the fits to (2) for the A particles on a log–log plot, where τ is reported as a function of $T - T_C$. We get similar results for B particles.

As the packing of the soft spheres increases there is a slowing down of the dynamics. The relaxation time in figure 2

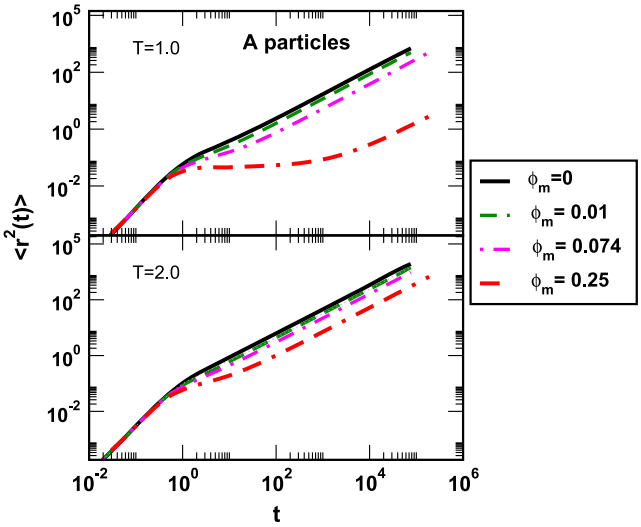

Figure 3. MSD of A particles as a function of time for $T = 2.0$ (bottom panel) and $T = 1.0$ (top panel) for the different packing fractions ϕ_m. The time is in LJ units (see text).

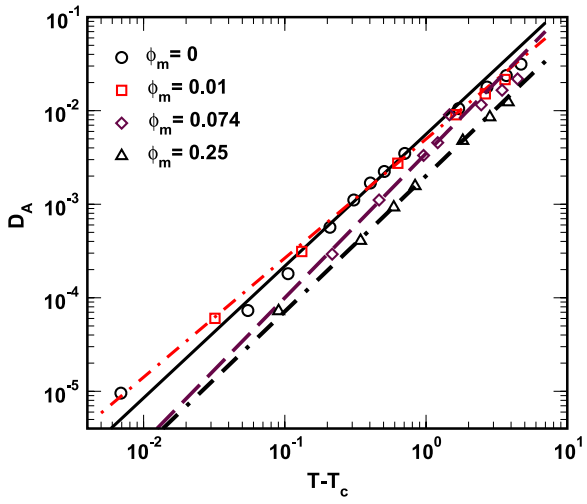

Figure 4. Diffusion coefficient of A particles for different ϕ_m as a function of $T - T_C$. The broken lines are the fit to the power law (3).

increases up to four orders of magnitude with the packing at the lowest temperature.

As further evidence of the effect of increasing confinement in figure 3 we report as a representative example the MSD for A particles for two temperatures and the different packing fractions. The onset of a caging effect for increasing ϕ_m is evident. At $T = 1$ the $\phi_m = 0.25$ case shows the typical behaviour of a liquid approaching the glass transition. After the ballistic regime at short time, the plateau indicates the rattling of the particle in the cage of nearest neighbours. At the end of the plateau the normal Brownian regime is recovered and the diffusion coefficient D can be estimated from the slope of the MSD, according to the Einstein relation. From our analysis the behaviour of D as a function of T close to T_C is in agreement with the predictions of MCT, equation (3). Figure 4 is equivalent to figure 2. Here we extract from the fits of D versus $T - T_C$ values for the crossover temperature

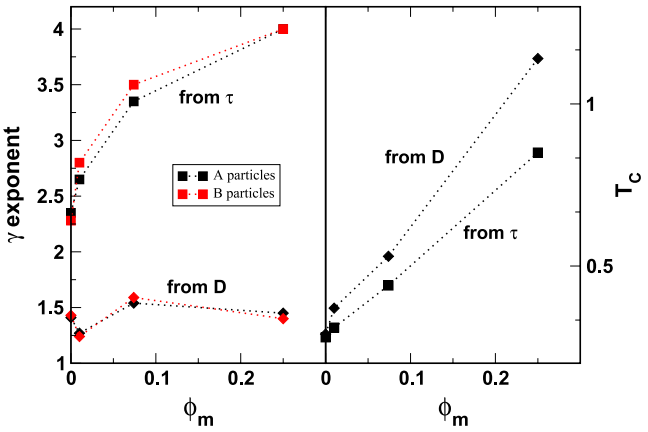

Figure 5. Left panel: exponent γ as obtained from the power law fits of τ and D for A and B particles. Right panel: MCT crossover temperature as obtained from D and τ.

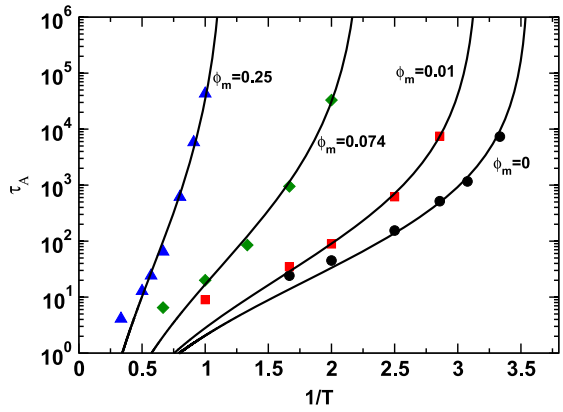

Figure 6. Relaxation time τ for A particles as a function of $1/T$ and for different ϕ_m. The bold lines are the fits to the power law (2).

and the exponent γ which are different from the previous ones obtained for τ.

The γ exponents extracted from the fits of equations (2) and (3) are shown in the left panel of figure 5 reported as functions of the packing fraction. For A and B particles we obtain very similar values in agreement with MCT but the exponents obtained from D are below the lowest limit predicted in MCT. The panel on the right, where T_C is reported as a function of ϕ_m, shows that the supercooled liquid phase region is restricted for the effect of increasing packing of the soft spheres.

The discrepancies between the values for γ and T_C extracted from τ and D can be attributed to the presence of hopping which affects more markedly the diffusion coefficient [38], as was found in simulations of the bulk LJBM [35–37]. It is clear that since the differences between the values obtained for T_C and γ from τ and from D increase with ϕ_m a higher packing enhances the hopping effects. Above or close to T_C hopping which is closely related to dynamical heterogeneities [43] becomes more relevant in confinement or in mixtures with large size asymmetry [44–47].

A further confirmation of the relevance of hopping effects in confinement comes from the plots of τ and D as

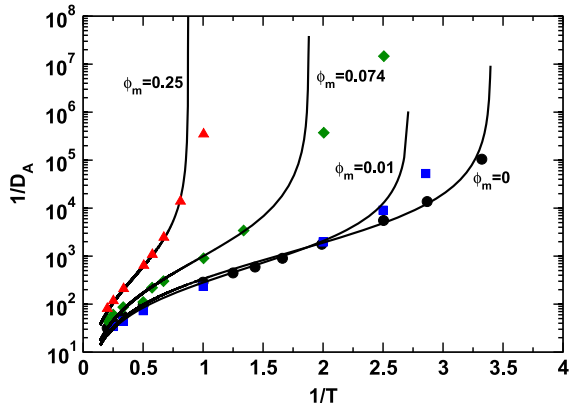

Figure 7. Inverse diffusion coefficient of A particles for different ϕ_m as a function of inverse temperature. The bold lines are fits to the power law (3).

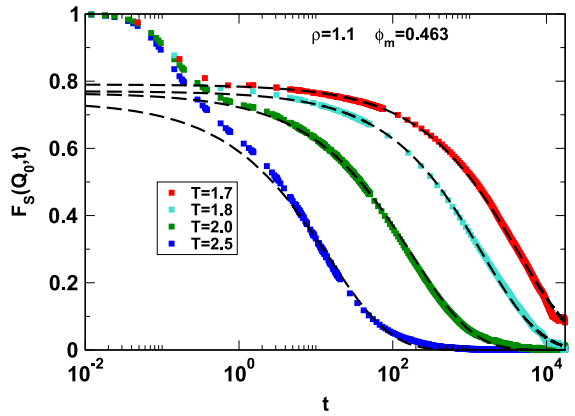

Figure 8. SISF for different temperatures and packing fraction $\phi_m = 0.463$. The broken lines represent the fits to the KWW law (see text). The time is in LJ units (see text).

functions of the inverse temperature. In figure 6 τ follows at low temperatures the power law also for $\phi_m > 0$, while from figure 7 it is evident that the behaviour of D deviates from the power law already at small ϕ_m. In the latter case it is possible to hypothesize a transition to an Arrhenius behaviour driven by hopping effects.

5. Higher packing confinement

The relevance of hopping effects at increasing confinement motivates simulations at even higher packing fractions. The simulations of the dynamical properties become computationally more demanding because of the slowing down of the dynamics. Due to the increase in the density of the soft spheres it is in fact more difficult to equilibrate the system if the inflation method is used. For this reason we decided to follow a different procedure in order to prepare our simulation cell.

Now we fix the σ of the soft sphere to the value $\sigma_m = 3.0$. Then for a given density of the liquid, in our case $\rho_f = 1.1$, we change the number of soft spheres N_m in order to obtain different values of ϕ_m. In this way the initial system is a three component mixture with LJ particles A, B and soft spheres M. The mixture must be equilibrated at high enough temperature.

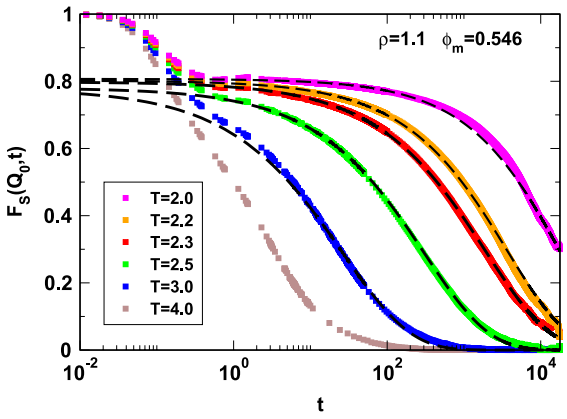

Figure 9. SISF as function of time for different temperatures and packing fraction $\phi_m = 0.546$. The broken lines represent the fits to the KWW law (see text). The time is in LJ units (see text).

During the equilibration runs there is a possibility that the system undergoes a demixing transition with an aggregation of the M particles in the same region of the simulation cell. This would represent a very specific type of configuration which is not appropriate to represent a liquid embedded in a QA matrix. Since the phase diagram of the system is unknown the only way to avoid this problem is to check the configurations and the thermodynamical parameters during the equilibration.

Once the mixture is equilibrated the M particles are fixed in their positions and equilibration runs of the confined LJBM are performed. With further runs of the equilibrated mixture it is possible to produce new configurations and produce other realizations of the simulation cell.

With this new procedure we started to perform MD of the confined LJBM at $\phi_m > 0.25$. We present here the first results obtained for $\phi_m = 0.364$, 0.463 and 0.546. The SISF obtained for $\phi_m = 0.463$ and $\phi_m = 0.546$ are shown in figures 8 and 9 respectively.

We observe a further decrease of the range of temperatures where the system is in a supercooled state with respect to the previous cases. Nonetheless in spite of the larger packing the α decay of the SISF can still be fitted with the KWW functions. Only for the lowest temperatures where it was possible to investigate the liquid is the fit more difficult to perform due to the fact that the SISF decay very slowly, showing that the system is approaching the glassy state. This is the main difference with respect to the SISF calculated for lower ϕ_m where there is not any signature of a dynamical arrest even at the lowest temperatures, as can be observed in figure 1.

From the fits of the SISF the relaxation times can be extracted; they follow the predictions of the MCT and are reported in figure 10 where for comparison we show also the case $\phi_m = 0.25$ already shown in figure 6.

The results for the B particles, not shown here, are equivalent to the ones for the A particles.

We observe that, at variance with the previous cases (see figure 6), now the points for the lowest temperatures for each of the three new ϕ_m investigated show the tendency to deviate from the power law of MCT. This is a clear indication that the hopping effects appear also in the behaviour of the relaxation

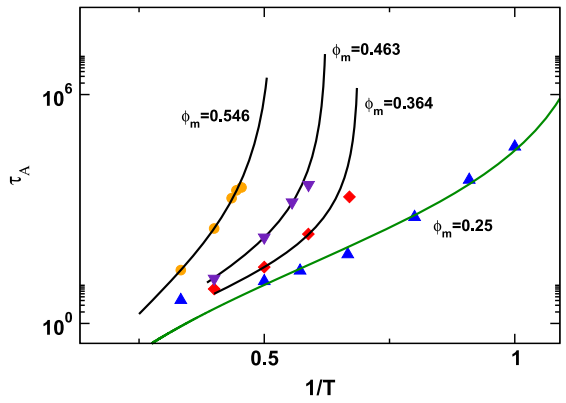

Figure 10. Relaxation time τ for A particles as a function of $1/T$ and for different ϕ_m. The bold lines are the fits to the power law (2).

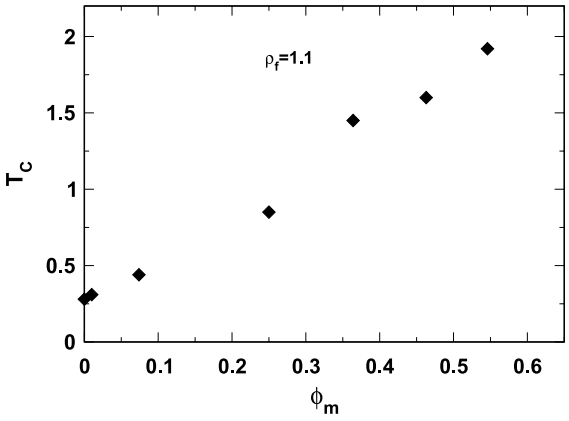

Figure 11. MCT crossover temperatures, obtained by power law fits to the relaxation time, as a function of increasing packing fraction.

time at a temperature that increases with the packing fraction. As a consequence the confinement could progressively mask the fragile behaviour of the glass forming liquid with a fragile to strong transition taking place at a temperature much higher than the bulk T_C.

In figure 11 we show the crossover temperature of MCT as a function of the packing fraction. The last three points in the plot are obtained with the new method. We note that the trend is linear in spite of the very strong confinement experienced by the mixture for the highest packing fractions.

6. Conclusions

In this paper we presented the results obtained from molecular dynamics simulations of an LJBM confined in matrices of randomly distributed soft spheres quenched in equilibrated configurations. We studied the systems upon supercooling to explore the dynamical single particle behaviour. Two methods have been used to build different realizations of the confining systems. The inflation method consists in changing a given number of LJ particles in soft spheres that are quenched after equilibration. This method was used to simulate the system for lower packing fractions. For higher confinement we equilibrated a three component system, where the soft spheres are the third component. After equilibration the soft spheres were quenched at their positions.

We found as a general trend that MCT is able to describe the dynamics of the LJBM at increasing confinement but hopping effects appear to be more relevant as the excluded volume due to the presence of the soft spheres increases. As a consequence the range of validity of the MCT decreases. The hopping seems to affect more the behaviour of the diffusion while the relaxation time seems to start to deviate from the MCT only for the highest packing fraction studied in this paper.

The increase of T_C as function of the increasing packing fraction seems to follow a linear trend.

Acknowledgment

We acknowledge the computational support given by the INFN RM3-GRID facilities at Roma Tre University.

References

[1] Debenedetti P G 1996 *Metastable Liquids: Concepts and Principles* (Princeton, NJ: Princeton University Press)
[2] Zorn R, Frick B and Büttner H (ed) 2000 *Proc. Int. Workshop on Dynamics in Confinement*; *J. Physique* IV **10** Pr7
Frick B, Koza M and Zorn R (ed) 2003 *Proc. 2nd Int. Workshop on Dynamics in Confinement*; *Eur. Phys. J.* E **12** 1
Koza M, Frick B and Zorn R (ed) 2007 *Proc. 3rd Int. Workshop on Dynamics in Confinement*; *Eur. Phys. J. Spec. Top.* **141** 3
[3] Alcoutlabi M and McKenna G B 2005 *J. Phys.: Condens. Matter* **17** R461
[4] McKenna G B 2007 *Eur. Phys. J. Spec. Top.* **141** 291
[5] Froltsov V A and Klapp S H L 2006 *J. Chem. Phys.* **122** 134701
[6] Götze W 2009 *Complex Dynamics of Glass Forming Liquids: A Mode Coupling Theory* (Oxford: Oxford University Press)
[7] Götze W and Sjögren L 1992 *Rep. Prog. Phys.* **55** 241
[8] Götze W 1999 *J. Phys.: Condens. Matter* **11** A1
[9] Gallo P, Rovere M and Spohr E 2000 *Phys. Rev. Lett.* **85** 4317
[10] Gallo P, Rovere M and Spohr E 2000 *J. Chem. Phys.* **113** 11324
[11] Attili A, Gallo P and Rovere M 2005 *J. Chem. Phys.* **123** 174510
[12] Gallo P, Pellarin R and Rovere M 2002 *Europhys. Lett.* **57** 212
[13] Gallo P, Pellarin R and Rovere M 2003 *Phys. Rev.* E **67** 041202
[14] Gallo P, Pellarin R and Rovere M 2003 *Phys. Rev.* E **68** 061209
[15] Varnik F, Baschnagel J and Binder K 2002 *Phys. Rev.* E **65** 021507
[16] Baschnagel J and Varnik F 2005 *J. Phys.: Condens. Matter* **17** R851
[17] Scheidler P, Kob W and Binder K 2000 *Europhys. Lett.* **52** 277
[18] Scheidler P, Kob W and Binder K 2004 *J. Phys. Chem.* B **108** 6673
[19] Sarkisov L and Monson P A 2000 *Phys. Rev.* E **61** 7231
[20] Rosinberg M L, Tarjus G and Stell G 1994 *J. Chem. Phys.* **100** 5172
[21] Madden W G and Glandt E D 1988 *J. Stat. Phys.* **51** 537
[22] Krakoviack V 2009 *Phys. Rev.* E **79** 061501
[23] Krakoviack V 2007 *Phys. Rev.* E **75** 031503
[24] Krakoviack V 2005 *Phys. Rev. Lett.* **94** 065703
[25] Krakoviack V 2005 *J. Phys.: Condens. Matter* **17** S3565
[26] Lomba E, Given J A, Stell G, Weis J J and Levesque D 1993 *Phys. Rev.* E **48** 233
[27] Given J A and Stell G 1992 *J. Chem. Phys.* **97** 4573
Given J A and Stell G 1994 *Physica* A **209** 495

[28] Kurzidim J, Coslovich D and Kahl G 2009 *Phys. Rev. Lett.* **103** 138303
[29] Fenz W, Mrygold I M, Prytula O and Folk R 2009 *Phys. Rev.* E **80** 021202
[30] Götze W and Sperl M 2004 *Phys. Rev. Lett.* **92** 105701
[31] Götze W and Sperl M 2002 *Phys. Rev.* E **66** 011405
[32] Mallamace F, Gambadauro P, Micali N, Tartaglia P, Liao C and Chen S-H 2000 *Phys. Rev. Lett.* **84** 5431
[33] Sciortino F, Tartaglia P and Zaccarelli E 2003 *Phys. Rev. Lett.* **91** 268301
[34] Chen S H, Chen W R and Mallamace F 2003 *Science* **300** 619
[35] Kob W and Andersen H C 1994 *Phys. Rev. Lett.* **73** 1376
[36] Kob W and Andersen H C 1995 *Phys. Rev.* E **51** 4626
[37] Kob W and Andersen H C 1995 *Phys. Rev.* E **52** 4134
[38] Gallo P, Attili A and Rovere M 2009 *Phys. Rev.* E **80** 061502
[39] Saika-Voivod I, Poole P H and Sciortino F 2001 *Nature* **412** 514
[40] Martinez L M and Angell C A 2001 *Nature* **410** 663
[41] Xu L, Kumar P, Buldyrev S V, Chen S H, Poole P H, Sciortino F and Stanley H E 2005 *Proc. Natl Acad. Sci.* **102** 16558
[42] Gallo P, Rovere M and Chen S H 2010 *J. Phys. Chem. Lett.* **1** 729
[43] Donati C, Glotzer S C, Poole P H, Kob W and Plimpton S J 1999 *Phys. Rev.* E **60** 3107
[44] Moreno A J and Colmenero J 2007 *J. Phys.: Condens. Matter* **19** 466112
[45] Moreno A J and Colmenero J 2006 *Phys. Rev.* E **74** 021409
[46] Moreno A J and Colmenero J 2006 *J. Chem. Phys.* **125** 164507
[47] Moreno A J and Colmenero J 2005 *J. Chem. Phys.* **123** 204505