Dynamical heterogeneity in glass-forming toluene: Comparison of bulk and confined conditions by quasielastic neutron scattering and molecular dynamics simulations

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Abstract

We investigate the presence of dynamical heterogeneities and their consequences on the incoherent intermediate scattering function $F_s(Q,t)$ of a molecular glass-forming liquid, toluene, in bulk and confined conditions. We show that the dynamical heterogeneity deeply affects the shape (stretching and plateau height) of the function $F_s(Q,t)$ and the mean square displacement when the slowest or the fastest populations are considered. Owing to the rigid character of the molecule and the remarkable agreement of the MD simulations with the quasielastic neutron scattering experiments, we extend our analysis to the interplay of translational and rotational motions in the relaxation processes. Since the existence of dynamical heterogeneities and a related cooperative length in the supercooled regime are postulated in many theoretical approaches of the glass transition phenomenon, the liquid is then confined into a pore of a few nano-meter diameter, where this characteristic length cannot extend beyond the pore size. The dynamics slow down when the size of the pore becomes smaller than the correlation length evaluated in the bulk with different methods (size effect on the diffusion coefficient, size of dynamical heterogeneities). An important increase of the stretching of the intermediate incoherent scattering function $F_s(Q,t)$ also appears. We show that the heterogeneous character of the dynamics increases when the liquid is confined due to the presence of a rigid surface.

Keywords: Neutron scattering; Dynamical heterogeneity; Glass transition; Molecular dynamics

1. Introduction

The existence of cooperative molecular motion in supercooled glass-forming liquids is commonly invoked [1] as the likely explanation for the dramatic increase of the viscosity as the liquid is cooled toward its glass transition. Cooperative motion is also commonly speculated in order to explain the observed stretching of correlation functions and the non-Arrhenius behavior [2,3] of the viscosity of most glass-forming liquids. Dynamical heterogeneities and associated cooperative behavior have been reported in various glass-formers [2,4], either experimentally near the glass transition temperature or with molecular dynamics simulations [5,6] well above this temperature. While no substantial increase of the static correlation functions is observed, the cooperative motions found via the dynamic heterogeneities are related to the expected increase of cooperativity postulated in several theoretical approaches.

The stretching observed in the time variation of various correlation functions like the incoherent intermediate scattering function (IISF) has been interpreted in term of heterogeneous dynamics. The wave-vector $Q$ depen-
dence of $F_{d}(Q,t)$ has also been interpreted in term of Gaussian and non-Gaussian dynamics [7], which in turn has been associated with the presence of dynamical heterogeneity. In complement to these studies, it appears of some importance to study directly the effect of dynamical heterogeneity on the function $F_{d}(Q,t)$; a function that is experimentally accessible via the incoherent dynamical structure factor via quasielastic neutron scattering experiments (neutron time of flight, backscattering or spin echo methods), and is often used for studying experimentally or numerically the dynamical properties of supercooled glass-formers. Molecular dynamics simulations have proved to be well adapted for this task [6,8,9].

Toluene is a relatively simple model for detailed studies of the normal and supercooled liquids down to the glass transition ($T_{g} = 117 \text{ K}$, $T_{m} = 178 \text{ K}$). For a better understanding of the special behavior of the correlations functions of glass-forming liquids, we propose realistic molecular dynamics simulations in a temperature region close and above the so-called dynamical critical temperature $T_{c}$ introduced by the Mode Coupling Theory, i.e., in the range where the dynamics change from an Arrhenius to a strong super-Arrhenius one. Toluene is a glass-former with extremely high fragility, i.e., it exhibits a very pronounced super-Arrhenius temperature dependence of the structural relaxation time when approaching the glass transition.

We investigate the effect of dynamical heterogeneity on the incoherent intermediate scattering function (IISF). In the framework of glass transition phenomenon, we show that dynamical heterogeneity deeply affects the IISF. The stretching of the IISF is increased by the presence of heterogeneity, i.e., a distribution of relaxation times in the liquid, involving slow and fast molecules. However, in the picosecond timescale we also study the coupling between several motions, rotational and translational, that is an alternative source of stretching. Since confined geometry has generated much interest because it is a possible operational procedure for extracting information on the existence and the size of a correlation length, the liquid is then confined into a nano-pore diameter, where this characteristic length cannot extend beyond the pore size. We observe important dynamical effects when the size of the pore is shorter than the correlation length evaluated in the bulk with different methods (size effect on the diffusion coefficient, size of dynamical heterogeneities). We therefore investigate the confinement effect on the dynamical heterogeneity and we show that surprisingly the heterogeneity increases when the liquid is confined.

2. Simulations

Our calculations on liquid toluene make use of the Jorgensen intermolecular potential model [10–12], which is one of the most realistic pair potentials for toluene in the literature. This potential is based on the Coulombic interaction with partial charges and a Lennard-Jones (LJ) intermolecular potential on each carbon and hydrogen atom of the molecule, the methyl group being modeled by only one site. The molecule is planar, excepting the methyl group, with a van der Waals radius of roughly 5.5 Å. The simulations are performed using a predictor–corrector Gear algorithm [13] with toluene modeled as a rigid molecule. Equations of motion for the 507 molecules are solved within the quaternion formalism [13] using classical mechanics. The time step was set to 1 fs. The reaction field method [13] was employed to take into account long-range electrostatic interactions. As the dipolar moment of the molecule is very weak [14], a cut-off radius of 3.8σ (14.5 Å) was found sufficient for the calculation of these interactions. The simulations are performed at constant densities, in the (N,V,T) ensemble, the density of the system being adjusted to the experimental ones [15] at atmospheric pressure. The model reproduces many of the bulk properties of the experimental liquid. A very good agreement with static quantities such as the structure factor was already found with experimental data [16,17]. For the dynamics, the simulations also agree very well with the experimental data down to low temperature [9].

The fluid is then confined into a cylindrical tube of 15 Å radius. We start the simulation with a parallelepipedic, 34 Å wide and 68 Å high, equilibrated box of the bulk system. To create the confining tube, we then fix some of the molecules according to the position of their centers of mass in the box. These stopped molecules act as an external potential. With this procedure, no thermal interactions between the wall and the confined liquid are considered. The system is then equilibrated over a relatively long period of time before any calculation of the autocorrelation functions is carried out.

In the Markovian approximation, the self part of the Van Hove correlation function $G_{d}(r,t)$ has a Gaussian form. This function is defined by

$$G_{d}(r,t) = \left\langle \frac{1}{N} \sum_{i=1}^{N} \delta(r + r_{i}(t) - r_{i}(t_0)) \right\rangle$$

and $4\pi r^{2}G_{d}(r,t)$ represents the probability for a particle to be at time $t + t_0$ at a distance $r$ from its position at time $t_0$. The Fourier–Laplace transform of $G_{d}(r,t)$ with respect to the spatial coordinate leads to the incoherent intermediate scattering functions

$$F_{s,\text{con}}(Q,t) = \left\langle \frac{1}{N} \text{Re} \left( \sum_{i=1}^{N} \exp(iQ \cdot (r_{i}(t + t_0) - r_{i}(t_0))) \right) \right\rangle$$

and

$$F_{s}(Q,t) = \left\langle \frac{1}{\sum_{i=1}^{158} b_{i}^{2}} \text{Re} \left( \sum_{i=1}^{158} b_{i}^{2} \exp(iQ \cdot (r_{i}(t + t_0) - r_{i}(t_0))) \right) \right\rangle.$$

(2)
These functions do not depend on $t_0$ if the liquid is at equilibrium. $N$ represents here the number of toluene molecules in the simulation box and $b_i$ the neutron scattering length of atom $i$. In the first part of this article, the IISF $F_i(Q,t)$ will not depend on the direction of the wave-vector $Q$ as the fluid properties are isotropic, but it will depend on the direction of $Q$ when the liquid will be confined in the pore. We will then name $F_{i}^{c}(Q,t)$ the function $F_{i}(Q,t)$ with wave-vector $Q$ in the direction of the pore axis $z$.

Departure from the Gaussian form of $G_{i}(r,t)$ has been found in various glass-forming liquids and they are thought to reflect the presence of dynamical heterogeneities. Such deviations are usually characterized by the non-Gaussian parameter, which in three dimensions has the following expression:

$$\alpha_2(t) = 3\langle r^4(t) \rangle / 5\langle r^2(t) \rangle^2 - 1. \quad (3)$$

The non-Gaussian parameter reaches a maximum for a characteristic time named $t^*$. $t^*$ evolves with temperature and it is thought to be a characteristic of the heterogeneity. We define the mobility $\mu_{i,0}(t)$ of molecule $i$ at time $t_0$ within a characteristic time $t$, by the relation

$$\mu_{i,0}(t) = |r_i(t + t_0) - r_i(t_0)|/\langle r^2(t) \rangle^{0.5}, \quad (4)$$

where $\langle r^2(t) \rangle$ is the overall mean square displacement.

The mobility of atom $i$ at time $t_0$ is then defined as the normalized displacement of atom $i$ during a time $t$. We will omit in further discussion the time $t_0$ which will disappear in the mean statistical values. We then select atoms of high or low mobility for the calculation of dynamical heterogeneity. This selection is then dependent on the time $t$ chosen for the definition of the mobility $\mu(t)$. When not specified, following Donati et al. [5] we use the time $t^*$ corresponding to the maximum of the non-Gaussian parameter as the characteristic time in this procedure. We define here as most mobile (MM) the 5% molecules with largest mobility, and as least mobile (LM) the 5% molecules with lowest mobility.

3. Results

In previous works [9,16–18], it has been shown that the diffusion coefficient [9] and the structure factor [16,17] are well reproduced with this intermolecular potential model down to relatively low temperatures. In particular, we have previously found that the non-Arrhenius behavior of the diffusion coefficient [19] is well reproduced by our simulations [9]. This result [9] (absence of finite size effects for this simulation box size) suggests that the expected correlation length associated with the non-Arrhenius behavior of the diffusion coefficient is shorter than the half size of the cubic box ($L_x = L_y = L_z = 40$ Å) used in the simulations [9]. The correlation length associated with this behavior has then to be shorter than 20 Å at a temperature of 160 K.

Fig. 1(a) shows the simulated IISF $F_i(Q,t)$ (continuous line) together with the experimental IISF function (points) for comparison. The wave-vector is $Q = 1.2$ Å$^{-1}$, which is near the maximum of the center of mass structure factor (1.3 Å$^{-1}$) and the temperature is 160 K, the lowest temperature investigated in this work. We observe a good agreement between the theoretical function and the experimental data. We observe the three characteristic time regimes of supercooled glass-forming liquids on the IISF. Between 0 and 1 ps, we observe the short time regime, the molecules moving relatively freely inside the cage formed by their neighbors. Then we observe the plateau regime between 1 and 10 ps. However, the legibility of the plateau is here strongly attenuated by the molecular rotational motion. Then between 10 ps and 2 ns, we observe the alpha relaxation regime, the molecule escaping the cage. We observe that the alpha relaxation regime is better reproduced with the simulations than the short time regimes. Because the rigid body approximation affects mostly short time regimes, we think that this approximation is partly responsible for this behavior.

Fig. 1(b) shows the rotational motion effect on the IISF function $F_i(Q,t)$: the IISF function $F_{\text{cond}}(Q,t)$ of the centers of mass (continuous line) together with the total IISF function $F_i(Q,t)$ (dashed line). $F_{\text{cond}}(Q,t)$ shows the relaxation associated with the centers of mass of the molecules, i.e., the translational relaxation. At variance to the total $F_i(Q,t)$ that takes into account the motion of each atom of the molecule, i.e., the whole translational and rotational motions of the molecule. We observe important differences between the two curves. Due to the rotational motion $F_i(Q,t)$ decreases faster than $F_{\text{cond}}(Q,t)$. This effect has to disappear when the translational motion will be large compared to the molecular diameter. However, with the conditions used in Fig. 1(b) ($Q = 1.2$ Å$^{-1}$, and $T = 160$ K) the rotational motion affects the IISF function $F_i(Q,t)$ for the whole time range of the figure. We also observe in Fig. 1(b), an important attenuation of the plateau when the rotational motion is taken into account. The plateau regime appears clearly for $F_{\text{cond}}(Q,t)$ and is attenuated in $F_i(Q,t)$. The rotational molecular motion increases the mean square displacement, because the motion is now the sum of the translation of the molecule and of its rotation. Within the Gaussian approximation we have (in three dimensions):

$$F_{\text{cond}}^{\text{Gauss}}(Q,t) = F_0 \exp(-Q^2 \langle r^2(t) \rangle / 6). \quad (5)$$

Equation (5) shows that an increase in $\langle r^2(t) \rangle$ results in a decrease of the IISF function $F_i(Q,t)$. Within the plateau time regime the molecule is trapped inside the cage constituted of its neighbors. Within this regime the translational motion is then limited by the size of the cage.
Because the size of the cage is comparable to the diameter of the molecule, the mean square displacement is strongly affected by the rotation of the molecule within the plateau time regime. This increase of the mean square displacement results in a strong modification of the plateau of the IISF as seen in Fig. 1 (b).

Fig. 2 (a) shows the radial distribution function between centers of mass of: the mean molecules (continuous line), i.e., an average over all molecules, the most mobile (MM) molecules (full circles) and the least mobile (LM) molecules (empty circles), at a temperature of 160 K. The characteristic time used in the calculation of the mobilities is $t^* = 0.2 \text{ ns}$ at this temperature and corresponds to the maximum of the non-Gaussian parameter. We observe in Fig. 2(a) that, at a temperature of 160 K, the three radial distribution functions (RDF) differ. The RDF between the MM molecules is higher than the mean. This result, which decreases at higher temperature and disappears above $T_m$, may be interpreted as an aggregation of the MM molecules. We also observe the same behavior for the LM molecules. This result shows the presence of dynamical heterogeneity in supercooled toluene. We see in Fig. 2(a) that the radius of the aggregation is around 15 Å, for both the MM and the LM molecules. We notice that this correlation length is compatible with the correlation length that we have previously estimated from size effects on the diffusion coefficient ($R < 20 \text{ Å}$) [9].

Fig. 2(b) shows the IISF $F_{\text{com}}(Q,t)$ calculated for the mean molecules (continuous line), the MM molecules (full circles) and the LM molecules (empty circles). Usually, the characteristic time $t^*$ corresponding to the maximum of the intensity of the heterogeneity is chosen in the mobility $\mu(t)$ definition (4), that is used for the selection between molecules of different mobilities. The heterogeneous behavior of the liquid is, however, composed of molecules with different characteristic times. More precisely, the heterogeneous behavior corresponds to a continuous distribution of characteristic times, and lifetimes for the heterogeneities. Inside this distribution, $t^*$ represents the characteristic time of the maximum of the distribution, then the most probable value at a temperature $T$. However in the time evolution of the IISF the different heterogeneities will contribute differently at different times $t$ to $F_{\text{c}}(Q,t)$. Molecules aggregating with an heterogeneous behavior corresponding to a characteristic time longer than $t^*$ will for example contribute preponderantly to the long time part (for $t > t^*$) of the IISF $F_{\text{c}}(Q,t)$. Using $t^*$ as the only characteristic time in the mobility selection of the dynamical heterogeneity.
Fig. 2. (a) Radial distribution function between: the mean toluene molecules (line), the most mobile toluene molecules (full circles), and the least mobile toluene molecules (empty circles). The temperature is 160 K. The characteristic time $t^*$ used at this temperature in the definition of the mobility is $t^* = 0.2$ ns. (b) Intermediate incoherent scattering function (centers of mass) $F_{\text{com}}(Q,t)$ for: the mean toluene molecules (line), the most mobile toluene molecules (full circles), and the least mobile toluene molecules (empty circles). The wave-vector $Q$ is 1.3 Å$^{-1}$ and the temperature is 160 K. As described in the text, a continuous distribution of characteristic times has been used for this calculation. (c) Mean square displacement of the molecular centers of mass $\langle r^2(t) \rangle$ versus time at a temperature of 160 K, for: the mean toluene molecules (line), the most mobile toluene molecules (full circles), and the least mobile toluene molecules (empty circles). As described in the text, a continuous distribution of characteristic times has been used for this calculation.
will then artificially eliminate important contributions to the IISF. In order to avoid this effect and be more realistic we have used instead here a distribution of characteristic times, centered on \( t^* \). The IISF for the most mobile or least mobile molecules displayed here represents then an average between different contributions.

We observe that the IISF function corresponding to molecules of different mobility differ in shape and intensity. The function corresponding to the least mobile molecules is higher and less stretched than the mean IISF function. This IISF joins the mean function for long times and stays near the mean IISF function for the whole time regime. In contrast the function corresponding to molecules of high mobility is weaker and more stretched than the mean function. The stretching of this IISF appears here partly from the presence of different times in the selection of the mobility. We will discuss this point further. This IISF function does not join the mean function for long times and stays quite different from the mean function for the whole time regime. The heterogeneities of weak mobility appear then to be preponderant in the mean IISF function, its relaxation time and shape. While the heterogeneities of high mobility increase the stretching of the mean IISF. The alpha relaxation time associated to the heterogeneities of weak mobility appears in Fig. 2(b) to be longer than the mean relaxation time. While the alpha relaxation time associated to the heterogeneities of high mobility is shorter than the mean relaxation time.

In the Gaussian approximation the IISF evolution may be related to the time dependence of the mean square displacement \( \langle r^2(t) \rangle \) (Eq. (5)). Fig. 2(c) shows the mean square displacement \( \langle r^2(t) \rangle \) between centers of mass of: the mean molecules (continuous line), the MM molecules (full circles) and the LM molecules (empty circles). The MM and LM mean square displacements differ from the mean at the end of the plateau time regime when some molecules begin to escape the cage of their neighbors. The modification of the mean square displacement (or equivalently the mobility) is more pronounced for the MM than for the LM. This modification leads to a more pronounced plateau for the LM (and a least pronounced plateau for the MM). The same modification of the plateau regime may be observed on (and a least pronounced plateau for the MM). The same modification of the plateau regime when some molecules begin to escape the cage of their neighbors. The modification of the mean square displacement \( \langle r^2(t) \rangle \) (upper curve) or total contribution \( F_s(t) \) (lower curve) inside the bulk at a temperature of 160 K (Fig. 2(a)). Fig. 3 shows the centers of mass IISF in the direction of the axis of the pore together with the total IISF in the same direction at a temperature of 200 K. We also show in this figure, for comparison, the same functions inside the bulk at a temperature of 160 K. In a previous paper [9], we have found a strong slowing down when

![Intermediate incoherent scattering function versus time.](image)

The stretching of the MM molecules IISF, seen in Fig. 2(b), is then increased due to this dispersion of the mobilities.

We finally see in Fig. 2(c) that the heterogeneous dynamics appears at 160 K around 10 ps and finishes around 2 ns when the diffusive regime begins. Around 2 ns, the MM and LM mean square displacements reach then the mean square displacement of the mean molecules. The heterogeneous dynamics is maximum in Fig. 2(c) for \( t = t^* = 0.2 \) ns, a value that corresponds to the maximum of the non-Gaussian parameter.

Finally, we consider the liquid toluene confined in nano-pores of cylindrical shape. The liquid is then confined in a pore of 15 Å radius across. This radius corresponds to the size of the dynamical aggregation observed in the bulk at a temperature of 160 K (Fig. 2(a)). Fig. 3 shows the centers of mass IISF in the direction of the axis of the pore together with the total IISF in the same direction at a temperature of 200 K. We also show in this figure, for comparison, the same functions inside the bulk at a temperature of 160 K. Due to the anisotropy of the confined liquid dynamics, we have chosen in this case the wave-vector \( \mathbf{Q} \) direction along the pore axis \( z \).
liquid toluene was confined in the same thermodynamic conditions. We observe this slowing down in Fig. 3. Fig. 3 shows that the alpha relaxation of the IISF at a temperature of 200 K within the pore presents similarities with the alpha relaxation in the bulk at a temperature in between 160 K and $T_m = 178$ K (which corresponds in the bulk to the absence of plateau and to a rapid alpha relaxation). We also observe the apparition of a long time tail in the IISF, in agreement with experimental data [18] of toluene confined in nano-porous silicate of similar size. This tail may arise from the contribution of the glassy molecules we previously have found [9] in the vicinity of the wall.

Fig. 3 shows that the rotational contribution affects differently the IISF in the bulk and in the pore. Indeed the gap between $F_z^c(Q, t)$ and $F_z^v(Q, t)$ evolves differently with time in the bulk and in the pore. However, we have to notice that the IISF corresponding to toluene confined in the pore, may result from the summation of different contributions. Liquid in the vicinity of the wall, experiences strong surfaces effects, while in the center of the pore the dynamics is less affected by the surface. It is interesting to note that the long time tails of the functions $F_z^c(Q, t)$ and $F_z^v(Q, t)$ are very different. This result may be interpreted as a preponderance of rotational motions for molecules trapped at the surface of the pore, in agreement with hopping rotational motions observed in previous simulations [9].

In Fig. 4, we compare the IISF (COM) in the direction $z$ of the pore axis, for the mean molecules (continuous line), the MM molecules (full circles) and the LM molecules (empty circles) at a temperature of 200 K. In order to discriminate between the liquid near the surface of the pore which experiences strong surface effects and the rest of the liquid, we display in this figure the contribution of the IISF from the liquid in the center of the pore and inset the total IISF with surface effects contributions. Fig. 4 inset, compared to Fig. 2 shows an important increase of the dynamical heterogeneities when the liquid is confined in the pore. We also observe that the IISF associated with the LM molecules is not reaching the mean IISF for long times, as it was observed in the bulk. But if we eliminate the contributions of the surface to the liquid dynamics we observe in Fig. 4 that the differences with Fig. 2 decrease. However, the dynamics is still more heterogeneous than in Fig. 2 and this result is observed for a temperature which is 40 K higher than in Fig. 2. Molecules in the vicinity of the surface of the pore have a much more heterogeneous behavior than molecules situated at the pore center.

We observe that the time evolution of the IISF associated with the MM and the LM molecules is different from the time evolution observed in the bulk in Fig. 2. The IISF associated with the MM molecules is now less stretched than the mean IISF, if we omit the long time tail contribution.

4. Conclusion

We have investigated the effect of dynamical heterogeneity on the neutron incoherent intermediate scattering function (IISF) for bulk and confined supercooled toluene. We have shown that in the bulk dynamical heterogeneity deeply affects the IISF. The stretching of the IISF is increased by the presence of heterogeneity. We have also studied the effect of the rotational molecular motion on the IISF. We have found that, for bulk supercooled toluene, the rotational motion increases the stretching of the function and has important effects on the resulting IISF function. Molecular dynamics appears then as an invaluable tool in order to interpret the experimental IISF function. With the aim of breaking the dynamical correlation length, the liquid has then been confined into a pore of size shorter than the correlation length evaluated in the bulk with different methods (size effect on the diffusion coefficient, size of dynamical heterogeneities). We then have investigated the confinement effect on the dynamical heterogeneity.
We found that surprisingly to us the heterogeneity increases when the liquid is confined inside the pore.

References