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Properties of a confined molecular glass-forming liquid

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Abstract

We use molecular dynamics (MD) simulations to investigate the modification of the dynamic and static properties of liquid toluene when confined in cylindrical mesopores a few molecular diameters across. Due to the strong influence of the substrate on the dynamics of the confined liquid, we choose a procedure where no additional thermal interactions between the wall and the liquid are taken into account. We observe the characteristic oscillations of molecular density profiles (layering) when temperature and pore size are changed. Mean square displacements and intermediate incoherent scattering functions of the centre of mass of the molecules are calculated as functions of different distances from the wall along the principal axis of the pore z and along the perpendicular x - and y -directions. At 200 K the relaxations of the two correlation functions slow down by one order of magnitude as compared to the bulk, with a slightly more pronounced slowing down in the x -direction. This slowing down increases strongly when the wall is approached. However, we do not observe any layer-specific dependence of the dynamics, but instead a continuous change. When the molecules are arrested near the wall in the time window (1 ns) of the simulations, we find hopping processes.

1. Introduction

When a liquid is confined into a pore a few molecular diameters across, its properties are deeply modified. The cooperative length postulated by most glass transition theories [1] in order to explain the formidable increase of the viscosity near the glass transition will not be able to extend to distances greater than the pore diameter. This effect may then lead to a different dynamical regime, and then to indirect information on this length scale. Unfortunately, reality is more complex and the limited length scale is not the only mechanism to take into account when a supercooled liquid is introduced into a pore: the dimensionality can be changed from three to one dimension (for a tube), finite-size effects appear, interactions with the surface may lead to

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increased or decreased molecular motions depending on the respective natures of the wall and fluid, and isotropy is broken at least near the wall, leading to layering. However, confinement is still an extremely interesting probe in the context of the glass transition mechanism. Moreover, as a result of the ensemble of mechanisms involved, molecules confined into nanopores exhibit interesting new physical behaviours. An example is layering which has been observed in a variety of confined systems including films of rare gases, liquid metals, water, and organic liquids [6–12]. But the most important changes are found in the dynamics. Some materials show an increase of the glass transition temperature with confinement [6, 7] together with an important slowing down of the dynamics, while in others T_g has been found to be decreased [10] and the dynamics accelerated.

In this article we use MD simulations to investigate the modification of the dynamic and static properties of liquid toluene with confinement in mesopores; this work is carried out in parallel with a wide experimental investigation of confined toluene in pores of similar dimensions [2]. We study the observed layering as a function of the pore radius and temperature. We find that confinement induces a strong slowing down of the structural relaxation near the wall and the plateau time region appears at higher temperature than in the bulk. Nevertheless, we do not observe any layer-specific dependency of the dynamics, but instead a continuous change of the properties, such as the mean square displacements and the incoherent intermediate scattering functions (IISFs) of the centre of mass of the molecules from the centre of the pore to the wall. Finally, near the wall we find hopping processes, rotational mainly, while in the centre the dynamics is still liquid-like. This article is organized as follows. In section 2 we describe the calculation method, the model, and the data analysis; in section 3 we discuss the different results related to the density profiles, paying attention to the anisotropy of molecular mobility in selected layers equally distant from the wall, and section 4 gives our conclusions.

2. Simulations and model

Toluene is one of the simplest molecular, internally rigid, glass-formers ($C_6H_5-CH_3$, $T_g = 117$ K, $T_m = 178$ K), which is van der Waals bonded. Toluene is a glass-former with very low molecular weight and extremely high fragility, i.e. it exhibits a very pronounced super-Arrhenius temperature dependence of the structural relaxation time when approaching the glass transition.

Our calculations make use of the Jorgensen intermolecular potential model [13] 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 CH_3 methyl group being modelled with only one site. Of course, the methyl group is not rigidly attached to the phenyl ring and performs rapid rotation around its C_3 axis. However, we can neglect this internal motion in the time window and at the temperature of our simulations. The molecular shape corresponds to the experimental form factor obtained in an earlier work [3]. The molecule is planar, excepting the CH_3 group, with a van der Waals radius of roughly 5.5 Å.

The simulations are performed using a predictor–corrector Gear algorithm with toluene modelled as a rigid molecule. Equations of motion for the 507 molecules are solved within the quaternion formalism using classical mechanics. To take advantage of the cage effect in the dynamics, a multiple-time-step approach was used, choosing 1 fs for the first shell with a cut-off radius of 2.5σ and 10 fs for the outer shell with a cut-off radius of 3.8σ . This approach leads to an increase of the efficiency of the algorithm by a factor 3. With these time steps the simulation was checked to lead to a stable conservation of the total energy of the system. The reaction field method was employed to take into account long-range electrostatic interactions.

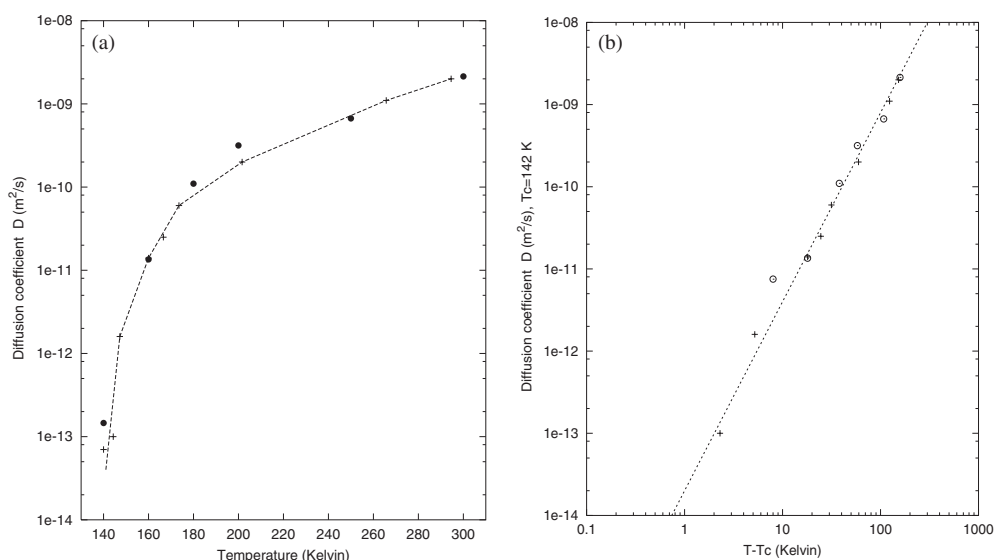


Figure 1. (a) Diffusion coefficient versus temperature. Circles show the simulations and crosses represent experimental data [17]. The dashed curve is a guide for the eyes. (b) Diffusion coefficient versus $T - T_c$. The line corresponds to a fit of a power law $(T - T_c)^\gamma$ with $T_c = 142$ K and $\gamma = 2.3$.

As the dipolar moment of the molecule is very weak [14], a cut-off radius of 3.8σ (14.5 \AA) was found to be 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 of the static quantities such as the structure factor was already found with experimental data [16]. For the dynamics, the simulations also agree very well with the experimental data down to low temperatures. In figure 1, the diffusion coefficient, calculated from the long-time part of the mean square displacement, is compared with the NMR measurements of Hinze and co-workers [17]. For the lowest temperature a simulation of the mean square displacement for times large enough to lead to a pure diffusive regime would take too long, and the coefficient was evaluated from a time-temperature rescaling procedure applied to the mean square displacement; this procedure was found to lead to a very good fit to the MSD of our calculations.

The fluid is then confined into a cylindrical tube of variable radius. We start the simulation with a parallelepipedic, 34 \AA wide and 68 \AA high, equilibrated simulation box of the bulk system. To create the confining tube we then fix some of the molecules according to the position of their centre of mass in the box. These stopped molecules act in the following calculations as the wall or equivalently as an external potential. With this procedure, no thermal interactions between the wall and the confined liquid are considered. Another advantage is that we begin the simulations with the same structure as in the bulk. We assume a wall interaction resembling the interaction in the bulk [7], in order to extract (mainly) size effects from the dynamics of the mobile molecules. The system is then equilibrated over a relatively long time period before any calculation of the autocorrelation functions is carried out.

3. Results

The simulations of the diffusion coefficient shown in figure 1 agree well with the experimental data over a wide temperature range (from 300 to 140 K) [5]. We can chose the simulation

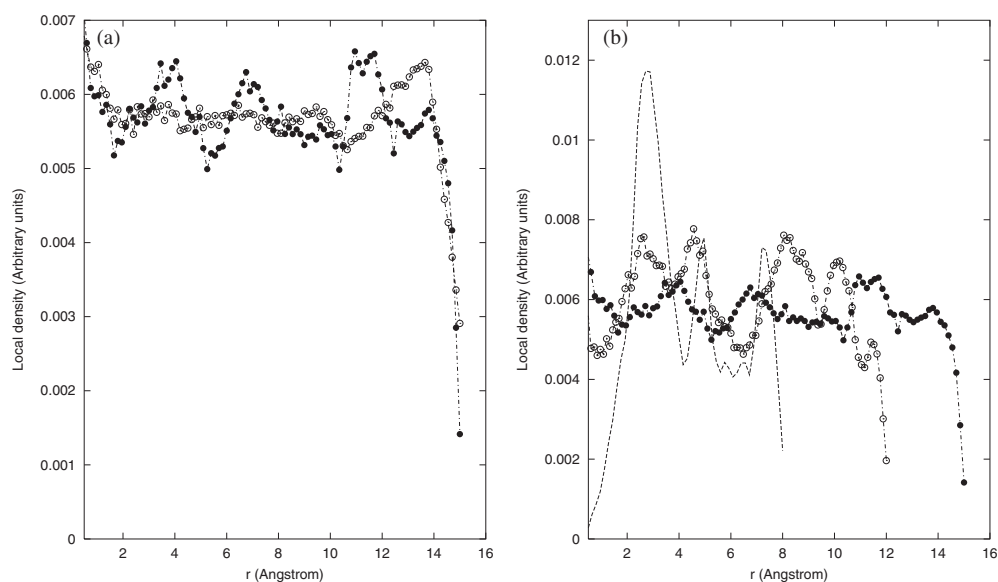


Figure 2. Local density profiles for liquid toluene. (a) At various temperatures in a pore of radius $R = 15$ Å. r represents the distance from the centre of the pore, and the local density is in arbitrary units. Full circles: 200 K; empty circles: 300 K. (b) At 200 K for different pore radii. Full circles: $R = 15$ Å; empty circles: $R = 12$ Å; dashed curve: $R = 8$ Å.

temperatures inside this wide range of temperatures. For comparison, the melting point of toluene is around 178 K and the mode-coupling theory (MCT) critical temperature is located around 142 K according to recent experiments [4]. In figure 1(b) we show a fit of our data with the predicted $(T - T_c)^\gamma$ behaviour of MCT. The Stokes Einstein viscosity calculated from our data is also found to follow the super-Arrhenius behaviour of the experimental data with temperature in the supercooled regime. The correlation length scale usually associated with this behaviour may thus be relatively well represented in our simulations.

In numerical simulations, walls of different kinds can be created. The most common are glassy silica (imitating Vycor or CPG) for comparison with experiments, infinite hard walls, or integrated LJ walls in a continuum for easier theoretical interpretation [6, 11, 12]. In any case, however, different effects are mixed in the simulations, as well as experiments, leading to difficulties in the interpretation of the observed properties. The most important of these effects are probably the direct liquid–wall interaction and the finite-size consequences for phase transitions. In order to try to decrease the effect of the wall–molecule interaction in our calculations, we use here a wall constituted of immobile bulk toluene molecules. This method has been previously used with confined LJ model systems [7]. In this case the wall has an amorphous structure with the local order of the liquid bulk at the same temperature, and the static interaction of the liquid with the wall is expected to be the same as inside the bulk.

In figure 2(a) we show the local density profiles of the centre of mass of the molecules for different temperatures and a pore size of 15 Å radius. We do not see in this figure any diffusion inside the wall, which is then compact enough to confine the whole set of molecules, despite its structure being analogous to that of the bulk liquid. This point is verified for all pore sizes of this work. Clearly a regular zigzag structure of the density oscillations is observed when the temperature decreases from 300 to 200 K. This layering effect has been found already for a large number of systems confined between different walls [6, 11, 12].

In dense materials like liquids, the minimum of the intermolecular potential is a preferred position for the neighbours. It induces a correlation of the positions of the molecules usually seen as oscillations in the radial distribution function. Under confining conditions, the distribution of the molecules reflected by the usual oscillations in the radial distribution function gives rise to the observed local density oscillations because of the anisotropy created by the wall.

In figure 2(a) we see that while at high temperature the local density oscillations are restricted to the liquid near the wall, for lower temperatures the layering increases and affects the whole pore. The same tendency is enhanced when the pore radius is changed: as shown in figure 2(b) at $T = 200$ K, the layering increases dramatically when the pore radius decreases. For the lower pore size ($R = 8$ Å) we even see a local density distribution reminiscent of capillary condensation. Layering is then inhibited by temperature or size increase. The amplitude and the period of these oscillations, but also the decay of the profile from the wall to the centre of the pore, depend strongly on the nature of the wall. When compared to the previous Monte Carlo analysis by Morineau [18] of toluene confined in a smooth and repulsive pore of similar shape, the observed layering is much less pronounced. Here the roughness of the wall and the attractive part of the wall–molecule interaction chosen decrease the layering [19] and minimize the surface effects generating the damped amplitudes and period, which does not match with the molecular diameter (5.5 Å). In the present case, the model of confinement should be more reliable for the study of the dynamics of glass-forming liquid. We then expect the dynamics to be, in the middle of the pore, relatively independent of the distance to the wall and closer to bulk conditions. We will see further that this is actually the case.

However, while the static behaviour of the layering is relatively well understood, the question of the dynamical behaviour has not been paid so much attention. Due to the particular cylindrical shape of the pore, one can consider the dynamics along axes parallel and perpendicular to the wall and the consequences of the anisotropy at several distances from the wall.

In figures 3 and 4, the autocorrelation functions calculated as a function of their distance d to the wall are shown. To this end we cut the cylinder radius into six equal parts of $\Delta r = 2.5$ Å each. The radius of the pore chosen for this figure is 15 Å and the temperature 200 K. We then calculate the autocorrelation function for each subcylinder of width Δr . For convenience, a molecule is considered to belong to a given subensemble where its centre of mass is located if it is inside at the initial time t_0 of the autocorrelation calculation.

This type of analysis is then only representative of the dynamics of a specific layer as long as only short and intermediate times are considered. For a long-time diffusion process the molecules move over several layers and distances from the wall, which gives rise to an averaged motion over different spatial environments. (With this procedure, the calculated dynamics and the corresponding relaxation time and stretching parameter are somewhat, modified because a molecule will find a change in regime when changing from one subcylinder to another.) Another approach will be to only consider the molecules that stay inside the subcylinder throughout the whole autocorrelation calculation. However, in this case while for short-time calculations the difference will be slight, for long times the statistic will decrease dramatically. The possibility of escape from one layer to another will also not have been taken into account in this procedure.

Various centre-of-mass mean square displacements at different distances from the wall are compared, in the z -direction, z being the axis of the pore, to the mean square displacements in the bulk state at 160 and 200 K. In order to take into account the anisotropy of the displacement inside the pore, the mean square displacement is calculated in a given direction: z or x . For an isotropic displacement, like in the bulk, $\langle r^2 \rangle = 3\langle z^2 \rangle$. We then have to remember that there is a factor 3 between the usual mean square displacement and $\langle z^2 \rangle$ which is calculated here.

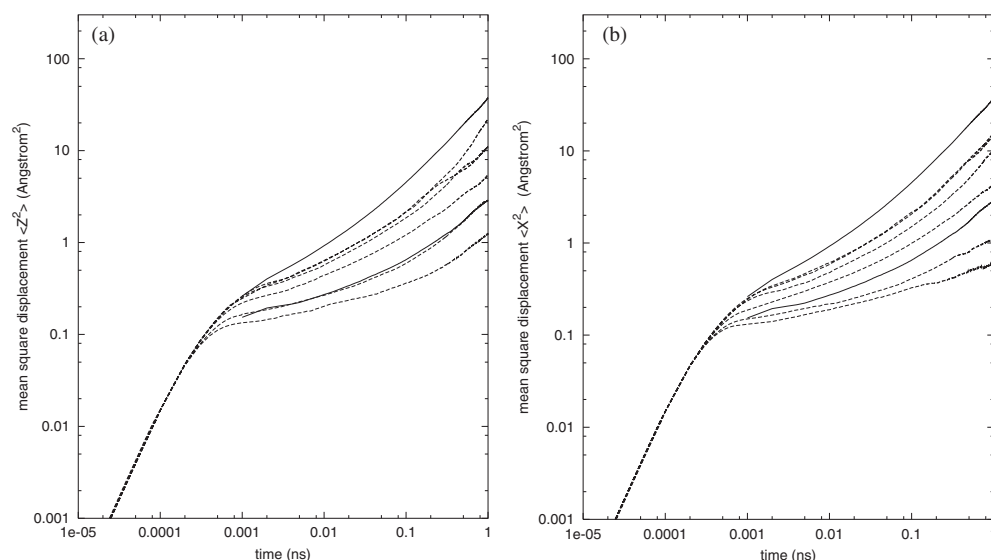


Figure 3. The mean square displacement (a) in the z -direction at different distances d from the wall, the distance decreasing from the top to the bottom in steps of 2.5 \AA . The temperature is 200 K and the pore radius 15 \AA . Continuous lines: bulk calculations of $\langle r^2 \rangle$ at 200 and 160 K . Dashed curves: calculations under confinement of $\langle z^2 \rangle$. (b) As (a), but in the x -direction: $\langle x^2 \rangle$.

When the distance from the wall increases, the long-time dynamics, related to the structural relaxation, changes gradually, while the short-time dynamics remains the same in all cases. Like in the bulk, we see two different time regimes in the correlation functions. For short times, the dynamics is governed by free motion of the molecules up to the picosecond timescale. Then the molecules start to feel the interactions with their neighbours and later the diffusion process begins. Between these two regimes a plateau develops, corresponding to the residence time of a molecule trapped in the cage formed by its neighbours.

We see in figure 3(a) that, near the centre, the dynamics is similar in shape to that of the bulk at 200 K , while near the wall, $\langle z^2 \rangle$ resembles the bulk behaviour at 160 K , with a connecting plateau not present or weakly detectable in the bulk at 200 K . When averaged over the whole pore, the long-time dynamics in the z -direction is then slower than that in the bulk at the same temperature. In the x -direction, i.e. perpendicular to the pore axis, the long-time motion is even more sensitive to the distance from the wall; in figure 3(b), near the wall the system seems frozen like the bulk at low temperature, i.e. below 140 K for this timescale.

When the temperature increases these differences decrease; the dynamics at the centre of the pore is less affected by the presence of the wall, more and more isotropic, and comparable to that of the bulk. Similarly when the pore radius decreases, the dynamics slows down more dramatically.

Investigating the pure diffusive geometrical effects with a random path calculation, one finds an increase of the mean square displacement in the radial direction.

While finite-size effects may slow the dynamics, the decrease of the dimensionality of the system near the wall and the wall–molecule interaction may also contribute. The wall of the present study, constituted of immobile bulk toluene, induces a kind of a rugged surface and generates at least a first intermediate quasi-immobile layer whose thickness may increase as temperature decreases.

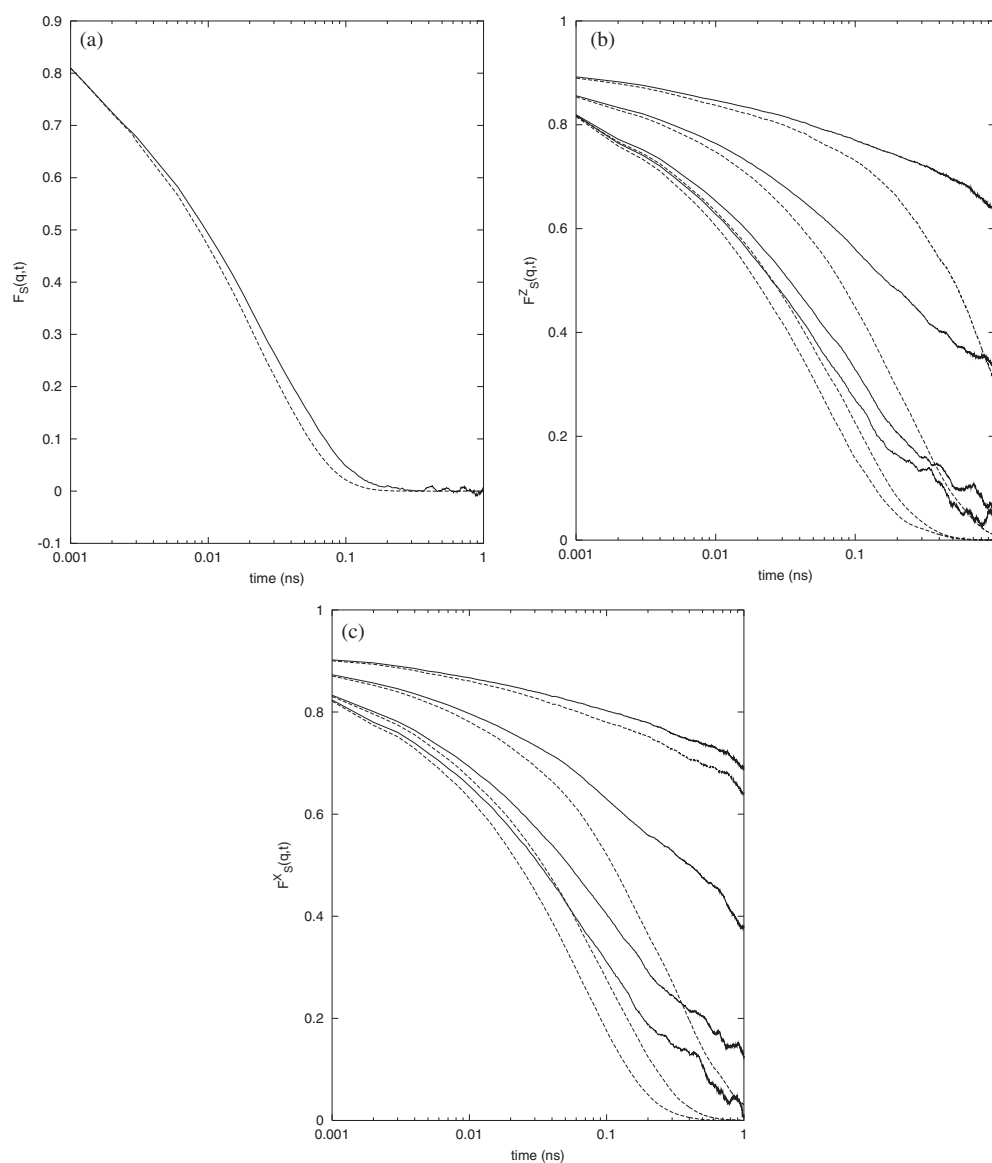


Figure 4. The IISF at a wavevector of 1.3 \AA^{-1} and 200 K (a) in the bulk liquid, (b) in the z -direction for different distances from the wall, (c) in the x -direction. In (b) and (c), from top to bottom, the distance from the wall increases in steps of 3.75 \AA . Dashed curves: Gaussian approximation calculations. Continuous curves: the complete calculation, as discussed in the text.

One can see in figure 3 that the overall dynamics in the pore is divided into two parts: at a maximal distance of 5 \AA from the wall the molecules are almost frozen, while all molecules located in the middle, i.e., from 5 to 15 \AA from the wall, exhibit the same dynamical behaviour, defining a pseudo-bulk pore of 20 \AA diameter. The direct effect of the wall–molecule interaction is expected to be relatively weak and finite-size effects may then play the major role in the slowing down [20] of the dynamics in the middle of the pore.

Similarly to the results found on confined water [6] we found an agreement with the power law MCT behaviour of the diffusion coefficient in the z -direction for molecules in the centre of the pore, with an increase of T_c from the bulk behaviour.

Another interesting quantity to investigate is the IISF, because it corresponds directly to the experimental data obtained by inelastic neutron scattering. This function describes the autocorrelation of the density fluctuations at the wavevector q :

$$F_S(\mathbf{q}, t) = \frac{1}{N} \operatorname{Re} \left(\sum_i e^{iq \cdot (r_i(t) - r_i(0))} \right). \quad (1)$$

Here $r_i(t)$ represents the position vector of the centre of mass of the molecule i at time t , and N the number of molecules. $F_S(\mathbf{q}, t)$ is directly related to the mean square displacement in the Gaussian approximation; for a given q in the z -direction we have

$$F_S^{\text{Gauss}^2}(q, t) = e^{-q^2 \langle z^2(t) \rangle / 2}. \quad (2)$$

However, this approximation fails clearly here because of the different dynamical behaviours inside the pore from the wall to the centre. Figure 4 shows these IISFs (at $q = 1.3 \text{ \AA}^{-1}$) for different distances from the wall in the z -direction and radial direction, and for the bulk liquid at the same temperature. Here, for better statistics, only four slabs in the cylinder are considered.

The dashed curves representing the Gaussian approximation calculation of the IISF are very different from the continuous lines which correspond to the non-approximated calculation of the IISF except for the bulk liquid. This discrepancy increases when we approach the wall. It is interesting to note that the non-Gaussian behaviour is much more important in the confined liquid than in the bulk. This behaviour leads to much slower relaxation functions than expected from the mean square displacement calculation. We conclude that the correlation between molecules increases consistently under confining conditions.

The stretching of the IISF functions is also an important experimental feature of the glass transition phenomenon. Stretching has been linked with the presence of heterogeneities in the dynamics, but it may also be attributed to the presence of layers and a surface effect. So it becomes interesting to investigate it as a function of the wall distance.

The stretching is found to be higher near the wall and to decrease when the distance from the wall is increased. The increased stretching near the wall may be expected as a result of the increase of the plateau region as the time for which a molecule stays inside the cage of its neighbours is increased in the observed slowing down.

We should also note from figures 3 and 4 that in the centre of the pore the first two or three radial steps have almost the same dynamics. In other words, we observe an equivalent dynamics in the centre within the first 10–15 \AA diameter in both directions, then it slows down dramatically when approaching the wall. This behaviour is seen more clearly in figure 5 where the alpha relaxation time is displayed versus the distance from the centre of the pore for a temperature of 200 K. The relaxation time is here defined as the time that it takes the IISF in the z -direction to decay to e^{-1} of its initial value. The alpha relaxation time is seen to be roughly constant near the centre of the pore, then increase exponentially when approaching the wall.

This behaviour is fairly similar to the two kinds of dynamics found in confined supercooled water [6]. The molecules at the centre behave in a more isotropic way—comparable to the behaviour in the bulk—and finite-size effects could be expected, while the molecules in the edge are predominantly affected by the wall. However, the relaxation time is larger than in the bulk, at all distances and in all directions, even at the centre, because the rigid surface effect persists throughout the whole pore with presumably a cooperativity length larger than

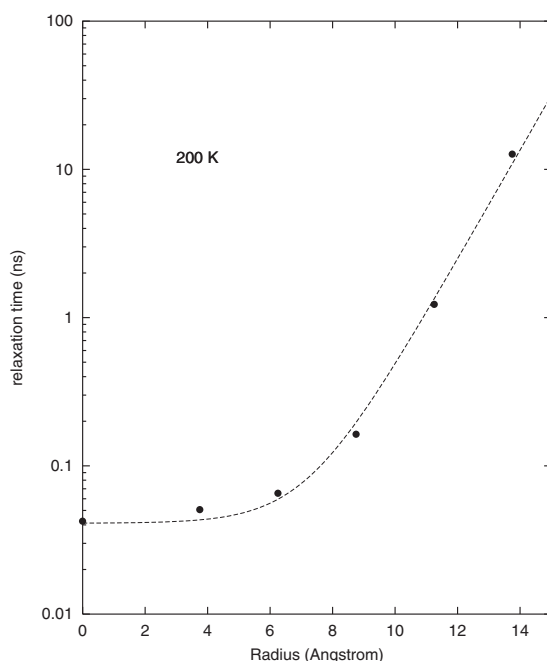


Figure 5. Alpha relaxation time for the z -direction versus the distance from the centre of the pore for a temperature of 200 K. The relaxation time is here defined by the time that it takes the IISF in the z -direction (figure 4(b)) to decay to e^{-1} of its initial value. Dashed curve: fit of the form $A + B \exp(Cr)$ with A , B , and C adjusted constants and serving as a guide to the eyes.

the pore radius of 3σ built in here. The surface induces the slowing down and no finite-size effects useful for the glass transition study are highlighted. Only at higher temperatures is a quantitative bulk-like timescale reached, while at lower temperature the cooperativity length induced by the immobile molecules at the surface will increase and an even slower behaviour will be observed.

From the above results, it is clear that near the wall the molecular motions are slower than in the centre by at least one order of magnitude in time. To investigate the motions near the wall, we have plotted in figure 6 the van Hove correlation functions which represent the probability for a particle to be at time t at a distance r from its earlier position at time 0:

$$G(r, t) = \frac{1}{N} \sum_i \delta(r - (|r_i(t) - r_i(0)|)). \quad (3)$$

In order to take into account the rotational motion of the molecule, we display here $G(r, t)$ corresponding to the deuterium atoms. These functions are plotted here for a time difference of 1 ns for different distances from the wall (near the wall, in the centre, and in between). For comparison we have plotted in figure 6(b) the same function in the bulk for different times at the same temperature. In the bulk, an enlargement of the van Hove function with time is usually observed; as the time is increased, the van Hove function is spread out due to the diffusion process. Inside the pore, the motion depends clearly on the distance from the wall. In the pore centre and around it, the 1 ns van Hove function behaves roughly as in the bulk but with a slower motion—even slower as we approach the wall. But around the wall the dynamics is different. We see several maxima, the second one increasing with time while the first is decreasing. This behaviour is typical of hopping processes. It involves the rotational motion

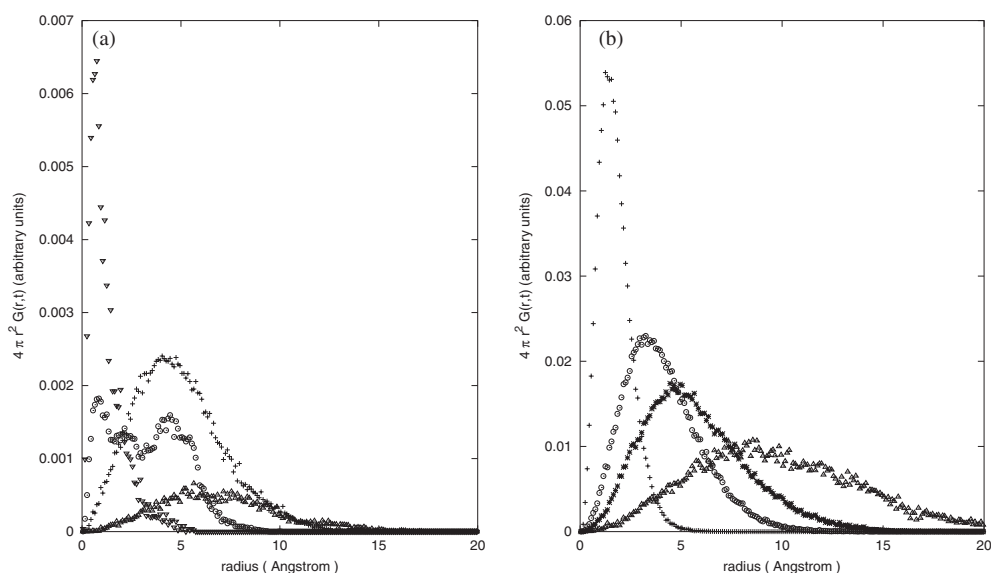


Figure 6. (a) The van Hove correlation function of the hydrogen atoms in a pore of 15 Å radius at a temperature of 200 K: $4\pi r^2 G(r, t)$ versus the distance r for different distances from the wall and a time difference of 1 ns. Circles: close to the wall; triangles: in the centre; crosses: in between. (b) The bulk behaviour of the van Hove function for different times ranging from 10^{-12} to 10^{-10} s at the same temperature.

of the molecule ring while no equivalent feature is observed for the centre-of-mass van Hove correlation function.

Surprisingly in figures 3 and 4 we do not see any significant change in the dynamics when crossing a layer. Instead, the mean square displacement increases smoothly from the wall to the centre of the pore. As shown at the beginning of this section, this may be related to the fact that layering and the dynamical property modification have different causes, the slowing down of the dynamics being due in our case to much more powerful factors than the layering effect. This however may not be the case for different kinds of wall.

4. Conclusions

In order to study the influence of temperature and confinement on the static and dynamic properties of a molecular glass-forming liquid, we have carried out MD simulations of toluene confined into pores a few ångströms in diameter (16–30 Å) constituted from an immobile bulk liquid structure. In agreement with previous results on molecular confinement, we found density oscillations, whose amplitudes depend strongly on the pore size and temperature. However, these oscillations are not very pronounced in the largest pores because of the specific wall–molecule contribution. More precisely, the roughness of the pore is of the order of the molecular diameter, and the diameter of the pore which corresponds to the distance between the centres of mass of the immobile wall molecules may be seen as a mean value of the various distances separating the atoms. As a result, the roughness of the wall considerably decreases the layering in our simulations.

Mean square displacements and correlation functions were calculated along directions parallel and perpendicular to the pore axis as functions of individual layers located at various distances from the wall. Mobility close to the wall is strongly reduced in both directions with

a slightly more pronounced effect in the radial one, and with a well defined plateau time region appearing only at low temperature in the bulk.

This slowing down depends on the position of the molecules inside the pore, making the averaged quantities (comparably to the experimental situation) apparently more stretched with a slower characteristic time. We did not observe any layer-specific dependence of the dynamics, but instead a smooth change between two distinct dynamical behaviours: molecules arrested at the wall and bulk like, but slower diffusive motion in the centre of the pore.

The length scale on which the influence of the wall on the liquid dynamics vanishes is of the order of 5 Å (which corresponds to roughly half the whole set of molecules) for a pore of 15 Å radius at $T = 200$ K, the dynamics of the inner molecules remaining isotropic but still slower by one order magnitude than that of the bulk at the same temperature.

Finally, near the wall we found hopping processes typical of frozen motions, while in the centre the dynamics is still liquid-like.

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