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Finite Size Effects and Cooperativity in a Model Diatomic Supercooled Liquid

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Abstract

We use large scale molecular dynamics simulations to investigate the relation between cooperativity and size effects in a simple diatomic supercooled liquid. We find that below a characteristic temperature the transport properties depend on the size of the simulation box. This effect then increases upon decreasing the temperature. For the model molecules constituting our liquid, the smaller box corresponds to the larger diffusion coefficient. Thus, the size effects increase the diffusion of the liquid with our molecules in opposition with previous results concerning silica and atomic soft molecules. As a result, the temperature dependence of the diffusion coefficient tends to an Arrhenius law for smaller boxes in our simulations. This result is in agreement with a cooperativity origin of non-Arrhenius behavior and size effects in fragile supercooled liquids, as a small box cutoff cooperative motions thus inducing a constant activation energy. To investigate that picture further we then study the size dependence of cooperative motions in our model liquid.

Keywords: Glass-transition, Supercooled liquids, Transport, Size effects, Confinement.

Introduction

Below their melting temperature, liquids present an universally large increase of their viscosity and relaxation times while decreasing the temperature. That dynamical slowdown, that appears without any significant structural modification of the liquid, is still an important unsolved mystery of condensed matter physics [1–4]. In some liquids (strong liquids in Angell's classification [5,6]) the viscosity, relaxation times, and the diffusion coefficient follow Arrhenius (exponential) laws of the form:

$$D = D_0 . e^{-E_a/k_B T}$$ for the diffusion coefficient. In this formula E_a is a constant activation energy. Note that the sign in the exponential is different for the relaxation times (or the viscosity). For other liquids, classified as fragiles[5,6], the viscosity increases faster (the diffusion decreases faster) than a pure exponential. Fragile liquids are usually described with the same exponential law, but with an activation energy that depends on temperature ($E_a(T)$ increases in fragile liquids when the temperature decreases). That increase of the activation energy is usually interpreted as a fingerprint of the appearance of cooperativity[7] in fragile liquids when supercooled. To be able to move, a molecule has to displace at least one surrounding molecule, leading to the activation energy and the Arrhenius dependence of strong liquids. The activation energy then increase in fragile liquids due to cooperativity as several molecules have to be displaced cooperatively, instead of only one. However, complicating somehow that simple picture, cooperativity also appears in strong liquids which best example is silica [8–11].

When confined inside a nano-porous material, the cooperativity's correlation length ξ cannot extend to distance larger than the size of the pore. As a result a study of the liquid properties dependence with the pore's size may lead to indirect information on the liquid correlation length(s). During the last decade a number of works [12–23] have been realized in that direction however they usually suffer from large boundary effects that originate from the wall and mask the size effects. Molecular dynamics simulations [24–27] can be used to bypass that problem [28–35], using a simple decrease of the simulation box size and periodic boundary conditions. Using that method, size effects have been found in fragile [28–30,33,35] and strong glass formers [31–34]. Molecular dynamics simulations (MD) permit to gain information on the motion of each molecule of the medium and is thus an invaluable tool to study condensed matter physics and unravel unexplained phenomena at the microscopic level [38–46]. Interestingly enough, despite the approximations inherent to simulations, molecular dynamics simulations display the unexplained viscosity increase of supercooled liquids in their approach to the glassy state. In this work we use molecular dynamics simulations to investigate the facts that suggest or are at odd with a cooperative origin to size effects and to the increase of the activation energy in supercooled fragile liquids.

Calculations

We model the molecules [47] as constituted of two atoms (i =

1, 2) that do interact with atoms of other molecules with the following Lennard-Jones potentials:

$$V_{ij} = 4\varepsilon_{ij}((\sigma_{ij}/r)^{12} - (\sigma_{ij}/r)^{6}) \qquad (1)$$

Where r is the distance between the atoms in interactions, and the parameters of the potential are:

$\varepsilon_{11} = \varepsilon_{12} = 0.5$KJ/mol, $\varepsilon_{22} = 0.4$KJ/mol, $\sigma_{11} = \sigma_{12} = 4.56$ Å and $\sigma_{22} = 4.33$ Å.

We use the molar mass M = 50g for each atom of the linear host molecule that we rigidly bond, fixing the interatomic distance to d = 2.28 Å. With these parameters the host does not crystallize even during long simulation runs [47]. As they are modeled with Lennard-Jones atoms, the potentials are quite versatile. Due to that property, the simulation results will be the same in dimensionless units that we choose to be: $r_d = r/\sigma_{11}$, $d_d = d/\sigma_{11}$, $t_d = t/(m\sigma_{11}^2/\varepsilon_{11})^{0.5}$, and $T_d = k_B T/\varepsilon_{11}$. The density is set constant in our calculations at $\rho = 1.615$ g/cm^3. When rescaled, or in dimensionless units, that density value is larger than the density of the original model [47], and thus leads to a more viscous medium. We use the Gear algorithm with the quaternion method [24] to solve the equations of motions with a time step $\Delta t = 10^{-15}$s. The temperature is controlled using a Berendsen thermostat [48]. We use periodic boundary conditions.

Results and Discussion

In Figure 1 we show the mean square displacement (MSD):

$$< r^2(t) > = \frac{1}{N.N_{to}} \sum_{i,t0}^{N,N_{to}} |r_i(t + t_0) - r_i(t_0)|^2 \qquad (2)$$

at different temperatures and for various simulation box sizes ranging from N=100 molecules (L/2 = 10.91 Å) to N=500 molecules (L/2 = 18.65 Å). In the formula, r_i stands for the position vector of the center of masses of molecule i. For the temperature T = 130K, the MSD doesn't depend on the size of the simulation box, indicating that no size effects are present on the diffusion in our model. In the picture of a cooperativity origin of size effects that result means that the typical length scale ξ of cooperative motions at that temperature is smaller than our smaller box half width ($\xi <$ L/2 = 10.91Å). When we decrease the temperature to T = 120K, size effects appear in the Figure 1b. The smaller box (N=100 molecules, L/2 = 10.91Å) displays the larger diffusion (i.e. the larger MSD). This result is in contrast with what is usually observed with confinement of liquids inside nanoporous materials. Confinement usually leads to an increase of the viscosity of the liquid and a decrease of the diffusion. However the presence of the confining pore's wall in that case affects strongly the dynamics of the liquid. Decreasing the temperature further (T = 110K) the size effects increase again, beginning to affect larger boxes. This result suggests that there is a characteristic length δ related to size effects and that increases when the temperature decreases. That result supports a cooperative origin of size effects as the cooperativity length scale ξ (in that picture δ≈ξ) universally increases when the temperature drops in supercooled liquids.

Note that in Figure 1, the size effects appear at the end of the plateau of the mean square displacement, when molecules begin to diffuse, escaping the cages constituted by their neighbors that imprison them. This result also comes in favor to a cooperative origin of size effects as cooperative motions are universally appearing on the same timescale (i.e. at the plateau ending). The smaller T dependence of the smaller boxes (the diffusion is larger for smaller boxes in Figure 1) implies that the diffusion follows a more Arrhenius-like evolution with temperature. Smaller boxes display smaller fragilities. That result agrees well with the picture of a cooperative origin to the non-Arrhenius behavior of fragile liquids.

In Figure 2 we show the radial distribution function at a temperature T=120K and for various box sizes. The Figure shows that there is no size effects on the structure of the liquid, as all curves superimpose. Thus size effects are mainly dynamical as the unexplained slowing down in supercooled liquids. This result suggests a common origin for both unexplained mechanisms. It comes in support of a cooperative motion (dynamical
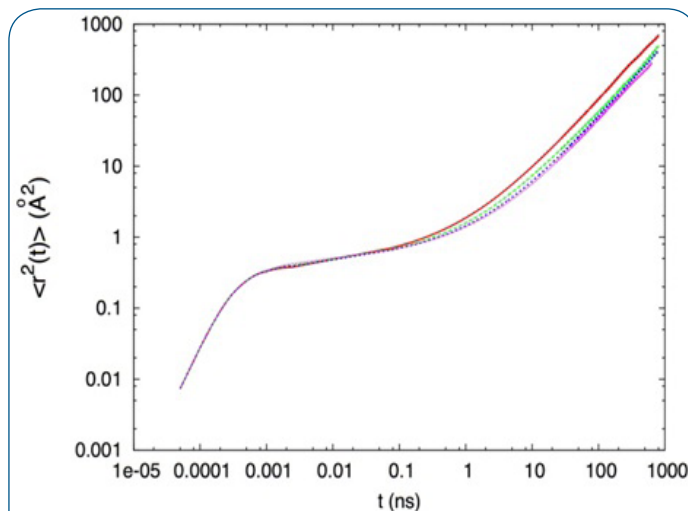

Figure 1(a): Mean square displacement of the molecules centers of masses for various simulation boxes sizes. The temperature is T=120K. From top to bottom (left of the figure) the sizes are: N=100 molecules (L/2 = 10.91Å, red curve); N=200 molecules (L/2 = 13.75Å, green curve); N=300 molecules (L/2 = 15.75Å, blue curve); N=500 molecules (L/2 = 18.65Å, pink curve); For smaller sizes (L/2 ≤ 10.5Å) the diffusion brutally stops and the system falls in the glassy state

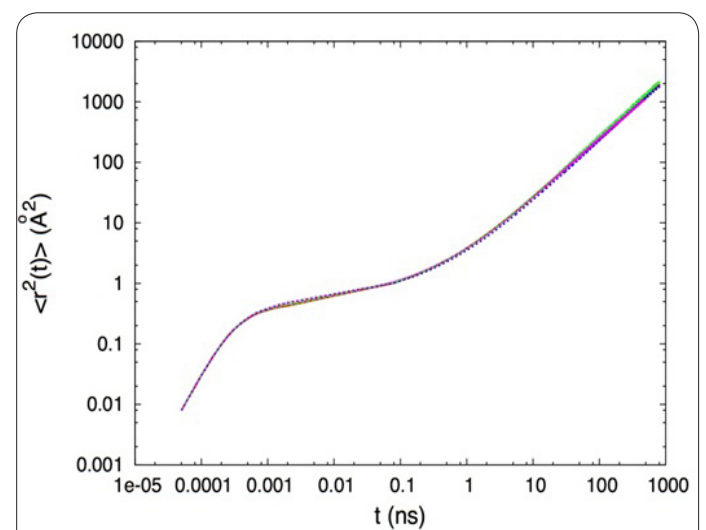**Figure 1(b):** As Figure 1a but at a temperature T=130 K. At this temperature we do not see any size effect on the Figure. The sizes are: N=100 molecules (L/2 = 10.91Å, red curve); N=200 molecules (L/2 = 13.75Å, green curve); N=300 molecules (L/2 = 15.75Å, blue curve); N=500 molecules (L/2 = 18.65Å, pink curve)
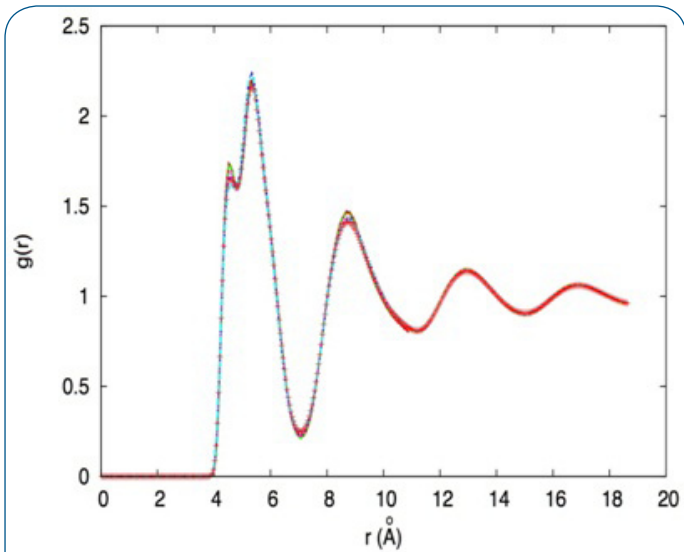
Figure 2: Radial distribution function between the molecules centers of masses for various simulation box sizes and temperatures. No size effects are visibles on the figure. Crosses: T=130K, N=500 molecules; Light blue: T=130K, N=100 molecules; Dark blue: T=120K, N=100 molecules; Pink: T=120K, N=500 molecules; Red: T=110K, N=100 molecules; Green: T=110K, N=500 molecules

heterogeneity) origin as that cooperativity is dynamical in nature.

In Figure 3 we show the Non-Gaussian parameter $\alpha_2(t)$ for various box sizes at a temperature T = 120K where size effects are present for the MSDs. The Non Gaussian Parameter:

$$\alpha_2(t) = (3 <r^4(t)>)/(5<r^2(t)>) - 1 \qquad (3)$$

where $<r^2(t)>$ is the mean square displacement described in formula (2), and

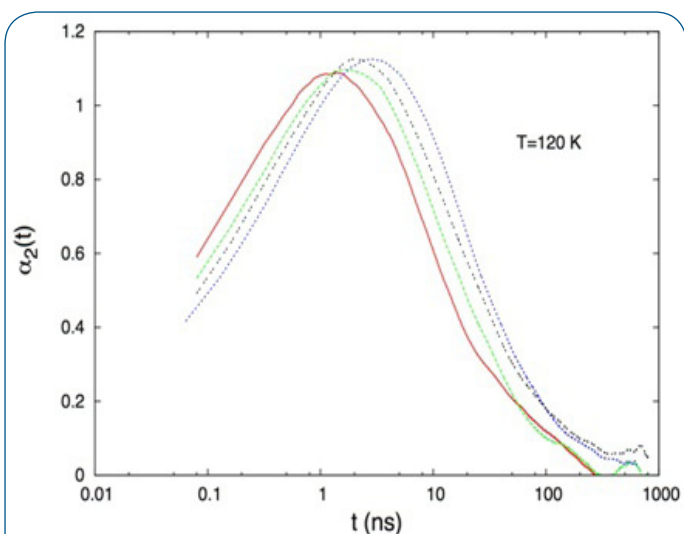$$< r^4(t) > = \frac{1}{N.N_{t0}} \sum_{i,t0}^{N,N_{t0}} |r_i(t+t_0) - r_i(t_0)|^4 \qquad (4)$$

Figure 3: Non Gaussian parameter for various simulation boxes. The simulation box sizes are from the left to the right: N=100 molecules (L/2 = 10.91Å, red curve); N=200 molecules (L/2 = 13.75Å, green curve); N=300 molecules (L/2 = 15.75Å, black curve); N=500 molecules (L/2 = 18.65Å, blue curve). T=120K

measures the discrepancy between the Van Hove correlation function and the Gaussian behavior that Brownian motions theory predicts for that function. As cooperative motions, called dynamic heterogeneity, induce the appearance of a tail in the Van Hove, due to molecules moving cooperatively faster than the average, the function $\alpha_2(t)$ is often used as a measure of the cooperativity in supercooled liquids. Figure 3 shows that the non-Gaussian parameter increases quite slightly with the size of the simulation box, while the characteristic time t* that corresponds to the maximum of $\alpha_2(t)$ increases more clearly with the box size. The increase of the characteristic time t* follows the previously observed increase of the relaxation time τ_α and is thus expected. Note that the maximum of the Non Gaussian parameter are located at the plateau ending of the mean square displacement as previously discussed. If the increase of the non-Gaussian parameter with the box size agrees with the picture of a cooperativity origin for the size effects and the non-Arrhenius behavior of fragile supercooled liquids, that increase is slight in comparison with other fragile glass-formers [28]. If compared to previous studies in silica, a prototype of strong glass formers, our results show a very different behavior. For example, the non-Gaussian parameter increases in silica when the box size decreases, in opposition with the results we find in our model fragile glass former. When the size of the simulation box decreases, the diffusion increases in that study while the diffusion decreases in silica. The non-Gaussian parameter doesn't show the expected decrease with the box size. A possible explanation is that the non-Gaussian parameter is affected by other physical phenomena masking its variations. In order to test that possibility, we have to measure the cooperative motions with a more direct method. To study in a more direct way the evolution of the dynamic heterogeneities with the box size, we now calculate the intensity $I^+(t)$ of the aggregation of the 5% most mobile molecules, where we define the mobility μ_i of molecule i at time t_0 for a characteristic time t as:

$$\mu i (t, t_0) = | r_i(t+t_0) - r_i(t_0) | \qquad (5)$$

Where $r_i(t)$ is the position vector of the center of masses of molecule i at time t.

We define as mobiles, the molecules with the larger mobilities, taking into account the 5% most mobiles only. We then define $I^+(t)$ as the probability $p_{mobile-mobile}(r<R)$ of a mobile molecule to be at a distance r, smaller than a characteristic distance R, of another mobile molecule divided by the same probability but for molecules of any mobility $p(r<R)$, and we subtract 1 from this value in order to obtain $I^+(t) = 0$ when there is no particular aggregation of the mobile molecules:

$$I^+(t) = p_{mobile-mobile}(r<R) / p(r<R) - 1 \qquad (6)$$

We choose here for R the value of the first minimum of the radial distribution function (R = 7Å), however we have verified that a different choice (for example R as the second minimum of the radial distribution function) leads to qualitatively similar results. We display our results in Figure 4.

The relative aggregation of mobile molecules $I^+(t)$ clearly decreases when the size of the simulation box decreases. We
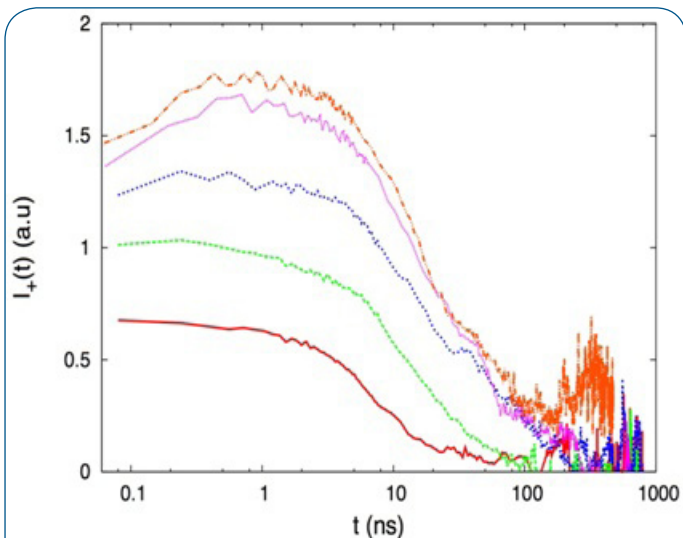
Figure 4: Intensity I+(t) of the dynamic heterogeneity related to the aggregation of the most mobile molecules. The simulation box sizes are from bottom to top: N=100 molecules (L/2 = 10.91Å, red continuous curve); N=200 molecules (L/2 = 13.75Å, green curve); N=300 molecules (L/2 = 15.75Å, blue curve); N=500 molecules (L/2 = 18.65Å, pink curve); N=600 molecules (L/2 = 19.8Å, orange dashed curve). The temperature is T=120 K

found a similar behavior using the least mobile molecules. These results are in agreement with a cooperative origin of the size effects in supercooled liquids.

Conclusion

In this work we have used large scale molecular dynamics simulations to investigate the temperature dependent finite size effects in a simple diatomic fragile supercooled liquid. Below a characteristic temperature (T < 130K in our model) the transport properties depend on the size of the simulation box. This effect then increases upon decreasing the temperature. We find that, for these molecules, the smaller box corresponds to the larger diffusion coefficient. In other words, the size effects increase the diffusion of the liquid in our simulations. The temperature dependence of the diffusion coefficient thus tends to an Arrhenius law for smaller boxes. This result is in agreement with a cooperativity origin of non-Arrhenius behavior and size effects in fragile supercooled liquids, as a small box will cutoff cooperative motions thus tending to a constant activation energy. To investigate that picture further we then studied the size dependence of cooperative motions (dynamic heterogeneities) in our model liquid, and we found that the cooperative motions decrease when the size of the box decreases, in agreement with the previous picture.

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