

## Structural relaxation in a supercooled molecular liquid

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**Abstract.** – We perform molecular-dynamics simulations of a molecular system in supercooled states for different values of inertia parameters to provide evidence that the long-time dynamics depends only on the equilibrium structure. This observation is consistent with the prediction of the mode-coupling theory for the glass transition and with the hypothesis that the potential energy-landscape controls the slow dynamics. We also find that the dynamical properties at intermediate wave number depend on the spatial correlation of the molecule’s geometrical center.

Dynamics in normal liquid states deals with orbits in phase space. Binary collisions and vibrations, for which the kinetic energy plays an important role, are elementary ingredients building the motion on microscopic time and frequency scales. In supercooled states, the system gets trapped in potential energy-landscape pockets for long times. This produces a separation of the long-time glassy dynamics —corresponding to the interbasin dynamics, *i.e.*, to the motion from one pocket to the other— from the microscopic dynamics.

In recent years the mode-coupling theory (MCT) for the glass transition has been developed [1]. One of its essential predictions is the independence of the glass-transition singularity, as well as of the long-time glassy dynamics, from the microscopic dynamics. This means that the glass-transition singularity and associated slow dynamics are completely determined by the statistics of the system’s orbits in configuration space rather than in phase space [2]. Such dynamics, determined solely by the equilibrium structure, is referred to as the structural relaxation. This MCT prediction agrees with the hypothesis that the potential energy-landscape controls the slow dynamics [3]. Indeed, an interesting characterization of the MCT critical temperature  $T_c$  in terms of geometrical properties of the landscape has been proposed [4, 5].

The issue of the independence of the long-time dynamics from underlying microscopic dynamics has been addressed for a binary mixture of Lennard-Jones particles [6]. In ref. [6], molecular-dynamics (MD) simulations have been performed based on Newtonian as well as stochastic dynamics, and the same long-time relaxation was observed. One of the main points of this letter is to explore whether such a property holds for molecular systems. This is nontrivial because the dynamics in molecular liquids involves rotational as well as translational motions, and there exist more than two time scales characterizing microscopic dynamics. Since these microscopic motions depend on molecule’s inertia parameters, we report in this letter

MD simulations for systems which differ in these parameters. Let us note that MCT for molecular systems —both the molecular theory based on the expansion in generalized spherical harmonics [7] and the site-site theory [8]— predicts the inertia-parameter independence of the long-time dynamics, and our work also serves as the first test of such a theoretical prediction.

Another motivation of the present study concerns the unusual wave number dependence of characteristic time in molecular systems. A strong correlation in the wave number dependence is usually observed between the so-called nonergodicity parameters (which specify the strength of the so-called  $\alpha$ -relaxation), the  $\alpha$ -relaxation times, and the static structure factor. This is found, *e.g.*, in hard-sphere system [9], Lennard-Jones binary mixture [10], water [11] and silica [12, 13], and is in agreement with the MCT prediction. The result found in a MD simulation study for a model of orthoterphenyl (OTP) [14] is unusual in that such a correlation is violated for wave numbers about half the position  $q_{\max}$  of the first sharp diffraction peak. It was suggested in ref. [14] that the unusual feature is caused by the coupling of the rotational motion to the center-of-mass motion. By changing inertia parameters, it shall be examined whether it is the coupling to the geometrical center or to the center of mass which matters.

We consider a model for OTP designed by Lewis and Wahnström (LW) [15] and a modified model which differs only in the mass distribution. The LW molecule is a rigid isosceles triangle. Each of the three sites represents an entire phenyl ring of mass  $m \approx 78$  amu, and is described by a Lennard-Jones sphere. Extensive studies on the dynamics and thermodynamics of the original model have recently been performed [14, 16]. In the modified model, the mass of the central site,  $m_c$ , and that of the two adjacent sites,  $m_s$ , are chosen so that  $m_c/m_s = 16$ , but with the total mass being unchanged,  $m_c + 2m_s = 3m$ . The center-of-mass position in the modified molecule nearly coincides with the position of the central site. The thermal velocity for the center-of-mass translation is the same for both models. However, the thermal angular velocities are increased for the modified model relative to the original one. Thus, one expects a considerable speeding-up of the reorientational motion, and, via the rotation-translation coupling, a considerable change in the complete microscopic dynamics. We have studied, performing MD simulations, both the original and modified systems composed of  $N = 343$  molecules at the density  $\rho = 1.083$  g/cm<sup>3</sup>, with the same procedure described in ref. [16].

Three normalized density correlators shall be considered:

$$\phi_q^X(t) = F_q^X(t)/F_q^X(0) \quad \text{for } X = N, Z, \text{ and } Q. \quad (1)$$

Here,  $F_q^X(t)$  are defined by  $F_q^X(t) = \langle \rho_q^X(t) \rho_q^X(0) \rangle / N$  in terms of the linear combinations

$$\rho_q^N = (\rho_q^1 + \rho_q^2 + \rho_q^3)/\sqrt{3}, \quad \rho_q^Z = (2\rho_q^1 - \rho_q^2 - \rho_q^3)/\sqrt{6}, \quad \rho_q^Q = (\rho_q^2 - \rho_q^3)/\sqrt{2}, \quad (2)$$

of the site-density fluctuations  $\rho_q^a = \sum_{i=1}^N \exp[i\vec{q} \cdot \vec{r}_i^a]$  ( $a = 1, 2, \text{ or } 3$ ) in which  $\vec{r}_i^a$  denotes the position of site  $a$  in the  $i$ -th molecule. (We use the convention that  $a = 1$  refers to the central site and  $a = 2, 3$  to the two adjacent sites.) Assuming equal scattering lengths, the correlator  $\phi_q^N(t)$  is directly related to the cross-section as measured in the coherent neutron scattering. The functional forms of  $\phi_q^Z(t)$  and  $\phi_q^Q(t)$  have been chosen so that their small-wave-number limits reduce to the 1st-rank reorientational correlators [17]. Dynamical features of  $\phi_q^N(t)$  for the original LW OTP have already been discussed in ref. [14].

We show in fig. 1 the correlators  $\phi_q^N(t)$  at  $T = 260$  K for wave numbers  $q = 15.2, 19.0$  and  $30.5$  nm<sup>-1</sup>. (We notice that the first peak in the static structure factor  $S_q^N = F_q^N(0)$  is located at  $q_{\max} = 14.6$  nm<sup>-1</sup>.) Circles and solid lines denote the results for the original and modified systems, respectively, and the time scale of the latter is rescaled by a factor  $\hat{t}_0 \approx 0.71$ , whose meaning will be discussed below. Except for  $t \lesssim 1$  ps, curves for the two systems coincide

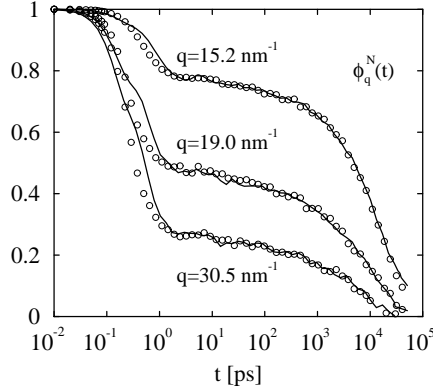


Fig. 1 – The correlators  $\phi_q^N(t)$  at  $T = 260$  K for wave numbers  $q = 15.2, 19.0,$  and  $30.5 \text{ nm}^{-1}$ . Circles and solid lines, respectively, refer to the results for the original and modified LW OTP, and the time scale of the latter is rescaled as  $t/\hat{t}_0$  with  $\hat{t}_0 \approx 0.71$ .

within the statistical errors, *i.e.*, the long-time dynamics is, up to the scale  $\hat{t}_0$ , independent of inertia parameters. Figure 2 shows corresponding results for  $\phi_q^Z(t)$  and  $\phi_q^Q(t)$ . While the short-time dynamics exhibits inertia dependence (see insets of fig. 2), the long-time dynamics is identical up to the same scale  $\hat{t}_0$ .

The findings in figs. 1 and 2 verify the following formulation of the glassy dynamics, as suggested by MCT [1, 2]: the microscopic dynamics determines a time scale  $t_0$  so that for  $t \gg t_0$  any correlator  $\phi_x(t)$  can be written as

$$\phi_x(t) = F_x(t/t_0). \quad (3)$$

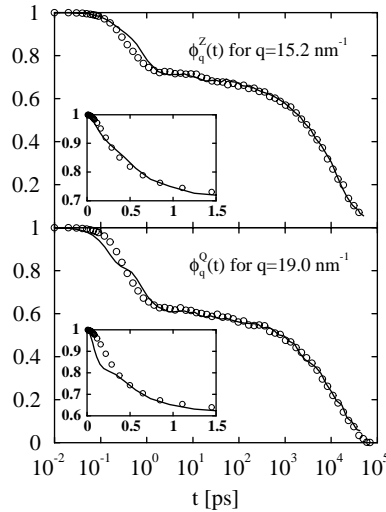


Fig. 2 – The correlators  $\phi_q^Z(t)$  for  $q = 15.2 \text{ nm}^{-1}$  (upper panel) and  $\phi_q^Q(t)$  for  $q = 19.0 \text{ nm}^{-1}$  (lower panel) at  $T = 260$  K. Circles and solid lines, respectively, refer to the results for the original and modified LW OTP, and the time scale of the latter is rescaled by  $\hat{t}_0 \approx 0.71$ . The insets show the short-time dynamics, *without rescaling the time scale for the modified system*, on the linear time axis.

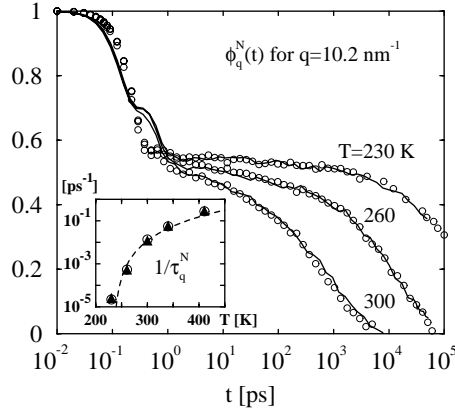


Fig. 3 – The correlators  $\phi_q^N(t)$  for  $q = 10.2 \text{ nm}^{-1}$  at three temperatures  $T = 230, 260,$  and  $300 \text{ K}$ . Circles and solid lines, respectively, refer to the results for the original and modified LW OTP, and the time scale of the latter is rescaled by  $\hat{t}_0 \approx 0.71$ . The inset exhibits the inverse of the  $\alpha$ -relaxation times  $1/\tau_q^N$  as a function of temperature:  $1/\tau_q^N$  for the original LW OTP are marked with open circles, while those for the modified system (rescaled by  $\hat{t}_0 \approx 0.71$ ) with filled triangles. The dashed line denotes the fit based on the prediction of MCT,  $1/\tau_q^N \propto (T - T_c)^\gamma$ , with  $T_c \approx 234 \text{ K}$  and  $\gamma \approx 2.76$ .

Here, the master function  $F_x(\tilde{t})$  is independent of the microscopic dynamics, and the scale  $t_0$  is common to all the correlators. The slow dynamics, as described by  $F_x(\tilde{t})$ , is solely determined by the potential energy  $V$  through the Boltzmann factor  $e^{-V/k_B T}$  (with  $k_B$  denoting the Boltzmann constant), *i.e.*, by the statistics of orbits in configuration space. The microscopic dynamics, which depends on inertia parameters, merely sets the scale  $t_0$  for the exploration of the potential energy-landscape. Thus, the factor  $\hat{t}_0$  used in figs. 1 and 2 can be understood as the ratio  $\hat{t}_0 = t_0^{\text{II}}/t_0^{\text{I}}$  of the  $t_0$ 's for the original ( $t_0^{\text{I}}$ ) and modified ( $t_0^{\text{II}}$ ) systems. The region where circles and solid lines coincide is the structural-relaxation part as described by  $F_x(\tilde{t})$ . The speeding-up of the rotational motion for the modified system, demonstrated in the insets of fig. 2, means that the potential energy-landscape can be explored faster. This explains why  $\hat{t}_0 < 1$ .

Figure 3 provides another test of eq. (3), where we plot  $\phi_q^N(t)$  for  $q = 10.2 \text{ nm}^{-1}$  at three temperatures close to the MCT critical temperature  $T_c \approx 234 \text{ K}$  [16]. The same  $\hat{t}_0 \approx 0.71$  has been used to rescale the correlators for the modified system. Since the microscopic dynamics can also depend on  $T$ , a smooth variation of  $\hat{t}_0$  with  $T$  is expected: for example, we checked that, by slightly modifying the value of  $\hat{t}_0$ , an even better agreement in the long-time dynamics is obtained for  $T = 300 \text{ K}$ . However, the temperature dependence of  $\hat{t}_0$  is rather small close to  $T_c$ , as can be seen from fig. 3. We note that, within MCT,  $\hat{t}_0$  should be evaluated at  $T = T_c$  [1, 2].

The dynamics in supercooled states exhibits two-step relaxation as shown in figs. 1-3: the relaxation toward the plateau, followed by the final relaxation from the plateau to zero (the  $\alpha$ -relaxation). The structural-relaxation region, where circles and solid lines coincide in figs. 1-3, is precisely the one for which MCT is derived and its applicability should be tested. We notice from figs. 1-3 that the approach toward the plateau, for which MCT predicts an asymptotic power law decay  $\sim t^{-a}$  ( $0 < a < 0.5$ ) [1], is almost completely masked by the microscopic dynamics. This implies that the most faithful tests of MCT should be performed just near the plateau and in the  $\alpha$ -relaxation regime. A similar conclusion was drawn in ref. [18] in a different context.

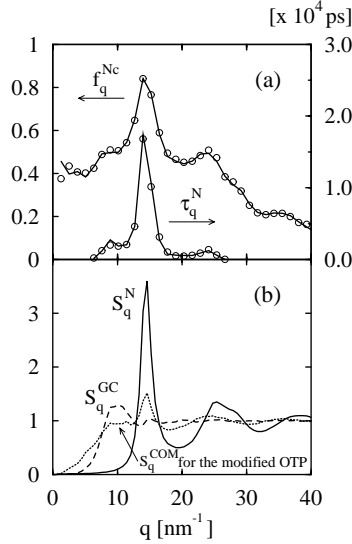


Fig. 4 – (a) The critical nonergodicity parameters  $f_q^{Nc}$  and the  $\alpha$ -relaxation times  $\tau_q^N$  for the correlators  $\phi_q^N(t)$ . The latter are calculated at  $T = 260$  K. Circles and solid lines, respectively, refer to the results for the original and modified LW OTP, and  $\tau_q^N$  for the latter are rescaled by  $\hat{t}_0 \approx 0.71$ . (b) The static structure factors at  $T = 260$  K. Solid and dashed lines, respectively, denote the site-site static structure factor  $S_q^N$  and the geometrical-center static structure factor  $S_q^{GC}$ , which are the same for both the original and modified LW OTP. For the original system,  $S_q^{GC}$  coincides with the center-of-mass static structure factor  $S_q^{\text{COM}}$ .  $S_q^{\text{COM}}$  for the modified system is denoted as dotted line.

The inset of fig. 3 shows  $1/\tau_q^N$  of the  $\alpha$ -relaxation times for the original and modified systems. In this work,  $\tau_q^N$  are defined by  $\phi_q^N(\tau_q^N) = 1/e$ . MCT predicts an asymptotic formula,  $1/\tau_q^N \propto (T - T_c)^\gamma$ , close to  $T_c$  [1]. The inset shows that the asymptotic formula describes well the result with  $T_c \approx 234$  K and  $\gamma \approx 2.76$  as estimated in ref. [16]. The exponent  $\gamma$  is uniquely related to the so-called exponent parameter  $\lambda$  [1]. The result indicates that, also for molecular systems,  $T_c$  and  $\lambda$  are independent of inertia parameters, in agreement with the prediction of MCT. Notice that this conclusion does not depend on the quality of the fit (*i.e.*, the choice of the values for  $T_c$  and  $\gamma$ ) since, after the rescaling by  $\hat{t}_0$ , the correlators  $\phi_q^N(t)$  and hence  $1/\tau_q^N$  for the two systems coincide within the statistical errors.

Equation (3) is based on the ideal MCT, whose validity is restricted to  $T > T_c$ . More precisely, eq. (3) is valid also below  $T_c$ , but according to MCT,  $F_x(\hat{t})$  for  $T \leq T_c$  would describe the arrest at the plateau [1], and does not properly account for the  $\alpha$ -relaxation in the simulation results, *e.g.*, the  $T = 230$  K result shown in fig. 3. The ideal MCT predicts the inertia parameter independence of the plateau height, and this can be confirmed from the figure. However, the  $T = 230$  K result also shows that, even for  $T < T_c$ , the  $\alpha$ -relaxation seems to be independent of inertia parameters. This implies the possibility of extending the formulation (3) to  $T < T_c$  including the whole  $\alpha$ -relaxation regime. Such a finding might help in developing theories for  $T < T_c$ . Let us note that this is also consistent with the energy-landscape description whose applicability is not restricted to  $T > T_c$ .

Next, we turn our attention to the wave number dependence of the  $\alpha$ -relaxation time for wave numbers around  $q_{\text{max}}/2$ . Figure 4(a) exhibits the critical nonergodicity parameters  $f_q^{Nc}$  and the  $\alpha$ -relaxation times  $\tau_q^N$  of the correlators  $\phi_q^N(t)$  for the original and modified systems.

Here,  $f_q^{\text{Nc}}$  are the plateau height in the two-step relaxation, and are obtained from the fit based on the vonSchweidler law with its first correction as in ref. [14]. Figure 4(a) shows that these quantities for the two systems are the same within the statistical errors. One also sees a clear correlation in the wave number dependence of  $f_q^{\text{Nc}}$  and  $\tau_q^{\text{N}}$ : there exist corresponding peaks and minima in these quantities.

The site-site static structure factor  $S_q^{\text{N}} = F_q^{\text{N}}(0)$  associated with  $\phi_q^{\text{N}}(t)$  is shown in fig. 4(b).  $S_q^{\text{N}}$  is the same for both the original and modified systems, since it depends only on the Boltzmann factor. For  $q \gtrsim 15 \text{ nm}^{-1}$ , the  $q$ -dependence of  $f_q^{\text{Nc}}$  and  $\tau_q^{\text{N}}$  correlates also with that of  $S_q^{\text{N}}$ . For  $q < 15 \text{ nm}^{-1}$ , on the other hand, such a correlation is not observed, and there is an unusual peak at  $q \approx 9 \text{ nm}^{-1}$  in  $f_q^{\text{Nc}}$  and  $\tau_q^{\text{N}}$  which does not exist in  $S_q^{\text{N}}$ . This is in contrast to results found, *e.g.*, in hard-sphere system [9], Lennard-Jones binary mixture [10], water [11], and silica [12, 13], for which such a correlation holds for the whole wave number regime.

In ref. [14], it was suggested that the unusual feature around  $q \approx 9 \text{ nm}^{-1}$  can be interpreted as being due to the coupling to the center-of-mass (COM) dynamics. This follows from the fact that the COM static structure factor,  $S_q^{\text{COM}} = (1/N) \sum_{i,j} \langle e^{-i\vec{q} \cdot (\vec{r}_i^{\text{COM}} - \vec{r}_j^{\text{COM}})} \rangle$  with  $\vec{r}_i^{\text{COM}}$  denoting the COM position, has a peak around  $q \approx 9 \text{ nm}^{-1}$  as shown in fig. 4(b). For the original model, the COM position is identical to the geometrical center (GC) defined by  $\vec{r}_i^{\text{GC}} = (1/3) \sum_{a=1}^3 \vec{r}_i^a$ . The latter is a structural property, *i.e.*, independent of inertia parameters, and the corresponding structure factor  $S_q^{\text{GC}}$ , defined in terms of the GC positions, is the same for the two systems in contrast to  $S_q^{\text{COM}}$  (cf. fig. 4(b)). Since fig. 4(a) shows that the peaks in  $f_q^{\text{Nc}}$  and  $\tau_q^{\text{N}}$  are also a structural property, we find —from the correlation between  $f_q^{\text{Nc}}$ ,  $\tau_q^{\text{N}}$ , and  $S_q^{\text{GC}}$ — that it is more appropriate to interpret the unusual peak around  $q \approx 9 \text{ nm}^{-1}$  as being caused by the coupling to the GC dynamics. Thus, the unusual peak reflects a property of the potential energy-landscape, a subtle interplay of the translational and rotational dimensions in configuration space. We notice that such a peak in the nonergodicity parameters around  $q \approx 9 \text{ nm}^{-1}$  can be found in the coherent neutron-scattering result for real OTP molecules, where no clear peak shows up in the static structure factor [19].

The position  $q \approx 9 \text{ nm}^{-1}$  where the unusual peak we discussed occurs is compatible with the inverse of the van der Waals radius  $r_W = 0.37 \text{ nm}$  for OTP molecule [20], *i.e.*, it is connected to the overall size of the molecule. It is interesting to note that a similar unusual peak was found in a model for polymer around wave numbers close to the inverse radius of gyration [21]. In ref. [21], the unusual peak is interpreted in terms of polymer specific properties. Such an interpretation might not be suitable, if the unusual peak —found in OTP and polymer— reflects the same physics. Thus, it will be a theoretical challenge to reproduce and explain such an unusual feature observed in molecular and polymer systems.

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