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Vibrational origin of the fast relaxation processes in molecular glass formers

S. Mossa^{1,2}, G. Monaco³ and G. Ruocco²

 ¹ Center for Polymer Studies and Department of Physics Boston University, Boston, MA 02215, USA
 ² Dipartimento di Fisica and INFM, Università di Roma "La Sapienza" Piazzale Aldo Moro 2, Roma, I-00185, Italy
 ³ European Synchrotron Radiation Facility BP 220 Grenoble Cedex, F-38043, France

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Abstract. – We study the interaction of the relaxation processes with the density fluctuations by molecular dynamics simulation of a flexible molecular model for o-terphenyl in the liquid and supercooled phases. We find evidence, besides the structural relaxation, of a secondary *vibrational* relaxation whose characteristic time, few ps, is slightly temperature dependent. This i) confirms the result by Monaco *et al.* (*Phys. Rev. E*, **62** (2000) 7595) of the vibrational nature of the fast relaxation observed in Brillouin Light Scattering experiments in o-terphenyl; and ii) poses a caveat on the interpretation of the BLS spectra of molecular systems in terms of a purely center-of-mass dynamics.

After the development of the Mode Coupling Theory (MCT) [1], which aimed to give a microscopic interpretation of the slowing-down of the dynamics which takes place at the liquidto-glass transformation, different experimental and numerical studies have been devoted to test its predictions, especially through the study of the density fluctuations correlation function, or of its space Fourier transform F(Q, t). These studies have covered a broad wave vector Q and temperature T range. In particular, the high-Q region has mainly been probed by numerical techniques [2] and inelastic neutron scattering spectroscopies [3], while the low-Qregion has been investigated by Brillouin Light Scattering (BLS), depolarized light scattering, and dielectric spectroscopy [4,5].

Despite this huge effort, the interpretation of the experimental tests of the main predictions of the MCT is still at the center of a strong debate, and a general consensus has not been reached yet. Indeed, a direct comparison of theoretical predictions with experimental results can be difficult, as it occurs in some light scattering experiments [4], in particular as far as the so-called β -region of the MCT is concerned. This is the time region where the first decay of F(Q, t), that is ascribed to the dephasing of the microscopic vibrational dynamics, merges with the earliest part of the decay associated to the structural (α) relaxation process. The MCT makes specific predictions on the shape of the F(Q, t) in this region, but additional contributions not yet included in the theory have to be taken into account in order to satisfactorily describe the experimental spectra [4]. Another debated issue is the recent observation of a flat background (constant loss) in the dielectric absorption spectra at few GHz [5], which seems at odds with some of the MCT predictions. In this case, the compatibility between the experimental results and the theory can be recovered but at the expense of admitting that not all variables reach the asymptotics which the MCT predicts to be universal [5].

Recently, studying the BLS spectra of o-terphenyl (oTP) [6], one of the prototypical fragile glass formers, some of us found evidences —besides the usual structural or α relaxation process— of a secondary relaxation, with a characteristic time τ_f lying in the ten picosecond time scale and weakly temperature dependent. This process lies in the frequency region where the features associated to the β -region are expected to show up. By comparing the BLS spectra in the glass and in the ordered crystalline phase, and by comparing the effect of this relaxation process on the longitudinal and transverse sound waves, the vibrational nature of the observed relaxation [7] has been suggested. If confirmed, this suggestion would indicate an important reason why the MCT predictions are not always retrieved in the light scattering experiments. Indeed the MCT is, up to now, formulated for monatomic or rigid molecules [8,9], the complexity of real non-rigid molecules —with all the processes associated to the internal vibrational dynamics— not yet being taken into account. The presence of a vibrational relaxation would indicate that the molecular glass formers are not suitable benchmarks to test the MCT on the short time scale. Indeed the presence of a vibrational relaxation dynamics lying in the 1–100 ps time scale would mask the spectral features predicted for the β -region. This considerations could partially explain the unsatisfactory consistency sometimes found between the MCT predictions and the BLS experiments [4].

Here we present a molecular dynamics simulation investigation of the relaxation processes active in oTP in a wide temperature range, spanning the normal and supercooled liquid region. Using the recent flexible molecular model for oTP [10,11], we investigate the coupling between the density fluctuations and the intra-molecular (vibrational) degrees of freedom. We find that i) there is a strong coupling between the density fluctuations and the vibrational excitations, and ii) that this coupling gives rise to a vibrational relaxation in the 10^{-11} s time scale. These findings strongly support the hypothesis suggested in ref. [7], and confirm the existence of a vibrational relaxation in oTP in the same frequency region where the signatures of the MCT β -region are expected. Moreover, by analyzing the effects of an external perturbation on the individual contributions to the intra-molecular interaction potential, we identify the phenyl-phenyl stretching as the internal vibration mainly responsible for such a relaxation. The absolute value of the relaxation time τ_f turns out to be a factor ≈ 3 shorter than the experimental value, a discrepancy that is tentatively explained on the basis of the classical nature of the MD simulations. Finally, we investigate the temperature dependence of τ_f , finding a behavior very similar to that observed in the BLS experiment [12].

We have studied a microcanonical system composed by 32 molecules (96 rings, 576 Lennard Jones interaction sites) enclosed in a cubic box with periodic boundary conditions. In the utilized model [10] the oTP molecule is constituted by three rigid hexagons (phenyl rings) of side $L_a = 0.139$ nm. Two adjacent vertices of the parent ring are bonded to one vertex of the two lateral rings by bonds of equilibrium length $L_b = 0.15$ nm. Each vertex of the hexagons is occupied by a fictitious atom of mass $M_{\rm CH} = 13$ a.m.u. representing a carbon-hydrogen pair (C-H). In the isolated molecule equilibrium position the lateral rings lie in planes that form an angle of about 54° with respect to the parent ring's plane.

The interaction among the rings pertaining to all the molecules is described by a site-site pairwise additive Lennard-Jones 6-12 potential, each site corresponding to the six hexagons vertices. Moreover, the three rings of a given molecule interact among one another by an *intra*- molecular potential, such potential being chosen in such a way as to preserve the molecule from dissociation, to give the correct relative equilibrium positions for the three phenyl rings, and to represent at best the isolated molecule vibrational spectrum. In particular it is written in the form $V_{\text{intra}} = \sum_k c_k V_k$, where each term V_k controls a particular degree of freedom. The contributions to the intra-molecular potential relevant to the present study are: i) the stretching along the central ring - side ring bonds (S), ii) the bending of the central ring - side rings bonds (B), and iii) the in-phase (R_1) and out-of-phase (R_2) rotation of the lateral rings along the ring-ring bond (1). The first two terms are modeled by springs, and the "interaction" with the other degrees of freedom (anharmonicity) is introduced by the site-site LJ potential of different molecules. The third term, on the contrary, has been modeled in a more realistic way. In this case the relevant variables are the two angles $\{\Phi_1, \Phi_2\}$ between the normals to the lateral rings and the parent ring plane. An *ab initio* calculation of the single-molecule potential energy surface as a function of these two angles has shown that two iso-energetic configurations exist separated by an energy barrier of height $V_S/k_B = 580 K$. The nature of the rotational motion at the temperatures of interest can be summarized as follows: the two side rings can pivot in phase around the bonds crossing from one minimum to the other degenerate one; at the same time they can perform librational out-of-phase motions. In order to represent this potential surface we express the in-phase rotation of the two side rings with a high-order (6th) polynomial and the out-of-phase rotation by a quadratic (harmonic) potential energy.

Other details of the intra-molecular and inter-molecular interaction potentials, together with the values of the involved constants, are reported in ref. [10]. Previous studies on the temperature dependence of the self-diffusion coefficient [10] and of the structural (α) relaxation times [10, 11] indicate that this molecular model is capable to quantitatively reproduce the dynamical behavior of the real system, but the actual simulated temperatures must be shifted by ≈ 20 K upward. In what follows, as our aim is to compare the simulation results with the experiments, the reported MD temperatures are always shifted by such an amount.

To investigate the effect of a long-wavelength density fluctuation —as those probed in a BLS experiment— on the intra-molecular vibrational dynamics we make use of a technique based on the following considerations. The characteristic time which a density fluctuation takes to relax towards equilibrium after interacting —via temperature— with one or more intra-molecular degrees of freedom can be shown to be proportional to the characteristic time which the energy of the involved internal degrees of freedom takes to relax towards equilibrium after a sudden density increase [13]. Moreover, if only few internal degrees of freedom are involved, the two characteristic times are essentially the same. While the former relaxation time is the one which is directly obtained in a BLS experiment, in the following we will determine the latter one, which is easier to work out by numerical simulation.

We then proceed as follows. After an equilibration run at a given temperature, we make a sudden density variation of the system ("crunch"), then we follow the time evolution of the intra-molecular potential energy during the subsequent evolution. As an example, in fig. 1 we report such a time evolution for T = 325 K and averaged over 2000 statistically independent crunches. The value of the internal potential energy is close to that pertaining to 12 harmonic oscillators (the number of internal degrees of freedom), 6RT = 16.2 kJ/mol, the slight deviation being associated to the anharmonicity present in the parameterizations of some of the internal degrees of freedoms. It is evident that, after the density change, the vibrational energy relaxes toward its new equilibrium value on a time scale of ≈ 6 ps, a value not far from

⁽¹⁾Another contribution to the intra-molecular potential is taken into account in the model, *i.e.*, the tilt of the ring-ring bonds. This contribution is constituted by two terms which are not relevant in this context and are not shown. It is worth noting, however, that their contribution to the total intra-molecular energy turns out to be negative.



Fig. 1 – Time dependence of the total intra-molecular potential energy after the density jump starting from a well-equilibrated configuration at T = 325 K. The data have been obtained averaging over 2000 realizations and the error bars represent the $\pm \sigma$ standard deviation of the different runs data.

the experimental one: $\tau_f \approx 20$ ps. We do not expect a much better agreement between these two values as i) the intra-molecular potential model has been parameterized to represent the vibrational spectrum of the isolated molecules — and not on the dynamics in the condensed phase —, and ii) the intra-molecular vibrational frequencies have values up to $\approx 500 \text{ cm}^{-1}$ ($\approx 720 \text{ K}$); therefore, at the investigated temperature, the quantum effects (population of the vibrational levels) certainly play a relevant role, and they are not considered in the present classical simulation. It is worth noting that, at this T, the α -relaxation time of density fluctuations determined by BLS is $\tau_{\alpha}^{\text{BLS}} \approx 100 \text{ ps}$, much longer than the time scale identified here. Also the rotational relaxational times turns out to be comparable with $\tau_{\alpha}^{\text{BLS}}$ [14].

Overall, we conclude from fig. 1 that there is definitively a coupling between the density fluctuations and the vibrational degrees of freedom -i.e., a vibrational relaxation is active in the system— and that the relaxation time favorably compares with the experimental findings.

In order to identify which one of the internal degree(s) of freedom is more efficiently coupled to the density fluctuation we cannot use the crunch technique, as a density jump simultaneously affects all the intra-molecular degrees of freedom. To selectively perturb a specific vibration, we proceed as follows. For each temperature, we equilibrate the system with a new set of elastic constants, where the constant of interest c_k is scaled to a new value $c_k^* = \lambda c_k$ (²), and store the final configuration. Then, starting from this configuration (t = 0), we perform two runs; we a) continue to evolve the system for ≈ 100 ps with the constants { c_n^* }, and b) evolve the system with the original set of elastic constants { c_n }. In this way run a) is an equilibrium run, while run b) is a run where, at t = 0, the system has been suddendly perturbed by a change in the Hamiltonian ($c_k^* \to c_k$) (³). After this perturbation is applied, we follow the time evolution of the specific term of the intra-molecular interaction potential energy, and measure the time needed to the energy to relax towards its equilibrium value. As an example, in fig. 2 (A-D), we report the time evolution of some of the terms V_k ($k = R_1, R_2, B, S$) for

 $^(^{2})$ We have used a value of $\lambda = 1.2$; this value has been chosen by some preliminary runs in such a way as to clearly observe a response to the introduced perturbation but to stay in the linear response regime.

 $^(^3)$ We have performed the runs applying the modification $c_k^* \to c_k$ (instead of $c_k \to c_k^*$) after the equilibration of the systems with c_k^* to always follow the relaxation dynamics of the "correct" (c_k) system. It is worth noting that, by modifying the elastic constants, we are not perturbing a specific vibration, as the latter are combinations of the different internal variables (bonds lengths and angles). However, as each molecular eigenmode mainly projects on one of the internal variables, we can anyway identify the vibrational modes responsible for the relaxation process.



Fig. 2 – (A) Signals (main panel) and relaxation function (inset) of the potential controlling the on-phase pivoting of the lateral rings at T = 370 K and $\lambda = 1.2$. (B) As above for the out-phase librations. (C) As above for the bending of the central ring - side rings bond. (D) As above for the stretching between the sides and central ring along the molecular bonds; it is worth noting that V_S decays on a time scale much longer than that of the other terms shown above.

the selected temperature T = 370 K (squares). The value of the energies measured in runs a) (open triangles) are also shown for comparison. Finally, in the insets, the difference $R_k(t)$ (normalized to unity at t = 0) between runs b) and a) are shown. As can be seen, all the potential term but V_S decay on a very fast time scale (≈ 100 fs or less followed by an oscillating tail that vanishes in ≈ 0.5 ps). The term V_S on the contrary decays on a much longer (> 1 ps) time scale. This term, controlling the stretching along the two bonds connecting the parent ring with the two side rings, is therefore the main candidate for the vibrational relaxation observed at few ten ps. It is worth noting that, as far as the ring-ring stretching vibration is



Fig. 3 – Relaxation functions $R_S(t)$ of the bond stretching potential at the four indicated temperatures.

Fig. 4 – Experimental (open circles, from ref. [12]) and MD (full diamonds) results for $\tau_f(T)$ reported in an Arrhenius plot. The MD data have been multiplied by a common factor F = 6 in order to show a T behaviour similar to that of the experimental data.

concerned, the stretching potential energy at long time in run b) (*i.e.*, with the set $\{c_n\}$ in the Hamiltonian) does not coincide with that of run a) (*i.e.*, with the set $\{c_n^*\}$). This indicates the presence of a relevant anharmonicity affecting this specific degree of freedom (in the absence of anharmonicity the two values are expected to be the same due to the energy equipartition).

The functions $R_S(t)$ are plotted in fig. 3 at selected temperatures, together with their best fit to an exponential decay. A slight but evident temperature dependence of the relaxation time is present. The T-dependence of the relaxation time derived from these fits is reported in fig. 4, together with the relaxation times for the fast process experimentally determined in ref. [12]. In this figure the MD data have been multiplied by a common factor F = 6 in order to emphasize that their T behavior is very similar to that of the experimental data. Both sets of data show an Arrhenius behavior at low T (with activation energy $\Delta E = 0.28 \pm 0.01 \text{ kJ/mol}$) and a different (steepest) trend at high T, where the fast relaxation process merges with the structural one. We notice the T-dependence agreement between the experimental data and the simulation after the appropriate rescaling. On the contrary, there is a discrepancy of a factor of about 6 between the MD and the experimental time scales. This difference could be explained, as noticed above, considering a non-perfect parameterizations of the intramolecular interaction potential and the fact that we expect strong quantum effects on the studied process. Moreover, in the present case further differences certainly arise from the different "perturbation" utilized in the MD simulation (changes of force constants) and in the experiment (density fluctuations).

In conclusion, by studying the coupling of external perturbations (a density fluctuation and a fictitious coupling constant modification) with the intra-molecular vibrations in a flexible model of oTP molecule we demonstrate i) the existence of a vibrational relaxation process with a non-negligible strength and a relaxation time in the few ps time scale; ii) that this relaxation process is mainly associated to the phenyl-phenyl stretching; and iii) that the relaxation time shows a temperature behavior very similar to that of the experimentally determined τ_f [6,7,12]. The quantitative discrepancies between the simulate and the experimental relaxation times can be tentatively assigned to the quantum nature of the real vibration, for which, at room temperature, $\hbar\omega_v/k_{\rm B}T \approx 2$.

The present findings give strong support to the vibrational origin of the fast relaxation process observed in oTP. It is tempting to generalize this conclusion to other systems where such a fast process has been observed (PC [15] and PB [16]). Given the depicted scenario, one should be extremely careful in drawing conclusion on either the validity, or the failure, of the MCT by the analysis of the isotropic light scattering spectra. This is especially true when analyzing the MCT β -region, as it lies at frequencies that coincide with the typical fast process ones and as its main features (susceptibility minima, *a* and *b* exponents, knees, etc.) can be masked by the fast process itself (⁴).

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 $^(^4)$ We note that an extension of MCT to non-rigid molecules would allow to compare the present results and the theory. The interference of the fast relaxation (due to vibrations) with the critical law predicted by MCT for rigid molecules is not an evidence that present MCT is wrong, but only that it is not general enough.