Vibrational origin of the fast relaxation processes in molecular glass-formers

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We study the interaction of the relaxation processes with the density fluctuations by molecular dynamics simulation of a flexible molecule model for o-terphenyl (oTP) 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\textbf{62}, 7595 (2000)] of the vibrational nature of the fast relaxation observed in Brillouin Light Scattering (BLS) experiments in oTP; and ii) poses a caveat on the interpretation of the BLS spectra of molecular systems in terms of a purely center of mass dynamics.

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After the development of the Mode Coupling Theory (MCT)\textsuperscript{[5]}\textsuperscript{[1]}, aimed to give a microscopic interpretation to the slowing down of the dynamics which takes place at the liquid-to-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 can be assigned to two broad classes, according to the value of the investigated wavevector $Q$. On one side the numerical techniques and the inelastic neutron scattering spectrosopies, that access the high $Q$ region, give a picture where the MCT predictions are basically demonstrated. On the other side the low $Q$ techniques as, for example, Brillouin Light Scattering (BLS), depolarized light scattering, or dielectric spectroscopy, depict a much less clear situation. For example, the recent observation of a flat background (constant loss) in the dielectric absorption spectra at few GHz\textsuperscript{[5]}, seems to contradict the MCT predictions on the same systems where the high $Q$ techniques confirm these predictions. A similar conflictual situation is also found in the case of the BLS experiments\textsuperscript{[3]}, in particular as far as the so called $\beta$-region of the MCT is concerned. This is the time region where the first decay of $F(Q, t)$, that could be ascribed to the dephasing of the microscopic vibrational dynamics, merge with the earliest part of the decay associated to the structural ($\alpha$) relaxation process. The MCT makes specific predictions on the shape of the $F(Q, t)$ in this region, but these predictions are not in agreement with the BLS, low $Q$, measurements\textsuperscript{[6]} whereas the high $Q$ neutron spectroscopy \textsuperscript{[8]} and molecular dynamics\textsuperscript{[9]} \textsuperscript{[10]} data support the validity of the MCT.

Recently, studying the BLS spectra\textsuperscript{[7]} of o-terphenyl (oTP), one of the prototypical fragile glass formers, some of us found evidences -besides the usual structural or $\alpha$ relaxation process- of a secondary relaxation, with a characteristic time $\tau_f$ lying in the ten picosecond time-scale and weakly temperature dependent. This process lies in the frequency region where the features associated to the $\beta$ region are expected to show up. By comparing the BLS spectra in the glassy and in the ordered crystalline phases, and by comparing the effect of this relaxation process on the longitudinal and transverse sound waves, it has been suggested the vibrational nature of the observed relaxation\textsuperscript{[3]}. If confirmed, this suggestion would indicate the reason why the MCT predictions are not always retrieved in the light scattering and dielectric experiments. Indeed the MCT is, up to now, formulated for monatomic or rigid molecules, the complexity of real non-rigid molecules -with all the processes associated to the internal vibrational dynamics- not 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 in the $\beta$-region. This considerations could explain the lack of consistency between the MCT predictions and the low $Q$ experiments.

In this letter 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\textsuperscript{[9-10]}, we investigate the coupling between the density fluctuations and the intramolecular (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.\textsuperscript{[3]} and confirm the existence of a vibrational relaxation in oTP in the same frequency region where the signatures of the MCT $\beta$-region are expected.
The 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 \([2]\). 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 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 exist two iso-energetic configurations 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 intramolecular and inter-molecular interaction potentials, together with the values of the involved constants, are reported in Ref. \([9]\). Previous studies on the temperature dependence of the self diffusion coefficient \([9]\) and of the structural \((\alpha)\) relaxation times \([9,10]\) indicated that this molecular model is capable to quantitative reproduce the dynamical behavior of the real system, but the actual simulated temperatures must be shifted by \(\approx 20\, K\) 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 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 intramolecular 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 2,000 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 clear that, after the density change, the vibrational energy relaxes toward its new equilibrium value in a time-scale of \(\approx 6\, ps\), a value not far from the experimental one: \(\tau_{\tau} \approx 20\, ps\). 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...
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spectrum of the isolated molecules -and not on the dy-
table, between the sides and central ring along the molecular bonds ;
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Overall, we conclude from Fig.4 that there is defini-
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levels) certainly play a relevant role, and they are not considered
in the present classical simulation.

The spectrum of the isolated molecules -and not on the dy-
the vibrational frequencies have values up to \( \approx 500 \text{ cm}^{-1} \)
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.

Overall, we conclude from Fig.4 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 of freedom(s) is more efficiently coupled to the density fluctuations we cannot use the crunch technique, as a
density jump simultaneously affects all the intramolecular degrees of freedom. In order to selectively perturb a specific vibration, we proceed as follows. After the equilibration run at a given temperature, the value of one of the elastic constants \( c_k \) is suddenly scaled \( (c_k \rightarrow c_k^* = \lambda c_k) \) with \( \lambda \) positive and small \([15]\).

After this perturbation is applied, we follow the time evolution of the specific term of the intra-molecular interaction potential energy and we measure the time needed to the energy to relax towards its new 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 the selected temperature \( T=370 \text{ K} \) (open squares). The value of the energies measured in runs without the perturbation (open triangles) are also shown for comparison. Finally, in the inset, the difference \( R_k(t) \) (normalized to unity at \( t=0 \)) between the perturbed and unperturbed time evolution are shown. As can be seen, all the potential term but \( V_S \) decay on a very fast time-scale (\( \approx 100 \text{ fs} \) or less followed by an oscillating tail that vanish in \( \approx 0.5 \text{ ps} \)). The term \( V_S \) on the contrary decays on a much longer (> 1 ps) time scale. This term, which controls 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, at variance with the other cases, the perturbed signal does not relax at the same value pertaining to the equilibrium signal; this indicates the presence of a relevant anharmonicity affecting this degree of freedom and that its equilibrium value depends on the density.

The functions \( R_S(t) \) are reported 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. [11]. In this figure the MD data have been multiplied by a common factor $F = 6$ in order to show the $T$ behaviour similar to that of the experimental data. Both sets of data show an Arrhenius behaviour at low $T$ (with activation energy $\Delta E = 0.28 \pm 0.01$ kJ/mole) and a different (steepest) trend at high $T$, where the fast relaxation process merges with the structural one. The agreement between the $T$ behaviour of the two sets of data is remarkable. 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 intra-molecular interaction potential and the fact that we expect strong quantum effects on the studied process. Moreover, in the present case, further differences can 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 $\tau_f$. 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, $\hbar \omega_0/k_B T \approx 2$. 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 [10] and PB [17]). Giving 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 light scattering or dielectric spectra. This is especially true when analyzing the MCT $\beta$-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.

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[12] An other contribution to the intramolecular potential is taken into account in the model, i.e. the tilt of the ring-ring bonds. Such terms are not relevant in this context.
[13] It is worth noting that the actual calculations have been performed applying the modification $c_k \rightarrow c_{k'}$ (instead of $c_k \rightarrow c_k'$), after the equilibration of the systems with $c_k$. In this way we always follow the relaxation dynamics of
the “correct” ($c_k$) system.

[14] Actually, 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.

[15] We have used a value of $\lambda = 1.2$; this value has been chosen by some preliminary run in such a way to observe clearly a response to the perturbation introduced but to stay in the linear response regime.

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