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Rotational dynamics in a simulated supercooled network-forming liquid

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Abstract

We discuss the coupling between rotational and translational motions in a simulated network forming liquid, i.e. the extended simple point charge (SPC/E) model developed to describe the behavior of water, a network of hydrogen bonds. We show that rotational correlators in supercooled states behave as predicted by mode-coupling theory (MCT) and present a simple modification of the standard MCT to describe the wave vector and time dependence of the center of mass (COM) correlators. We compare the predictions of the model with the numerical data, calculated from a molecular dynamics (MD) simulation.

1. Introduction

The ideal mode-coupling theory (MCT) [1,2] for supercooled liquids has been subjected to extensive tests in recent years, both from experimental [3,4] and numerical works [5–7]. As a result, there is now growing consensus in the scientific community that the theory can successfully describe the dynamics of liquids in the early supercooling regime, i.e. down to a cross over (critical) temperature, T_c, at which the so-called hopping effects become dominant [1,8]. Even though the theory was originally developed to describe the slow dynamics in simple liquids, i.e. liquids made by atoms or by molecules interacting through a spherically symmetric potential, experimental [3,9,10] and numerical [6,11–13] results have shown that molecular liquids also behave, at least qualitatively, as predicted by the theory. Unfortunately, a complete comparison between the theory and the experimental data for molecules of arbitrary shape could not be performed, because the original ideal MCT did not include orientational degrees of freedom. Important recent results have opened the way to a deeper understanding of the physics beyond the liquid to glass transformation of molecular liquids. An extension of the MCT equations to molecular liquids has been recently developed and predictions for the q-vector dependence of the non-ergodicity parameter, both for center of mass (COM) and angular correlators is now available for liquids composed of linear molecules [14,15] and for a single solute molecule in a simple solvent liquid [16]. A successful comparison between theoretical predictions and numerical data for a liquid of Lennard–Jones dumbbells encourages further investigations in this direction [11,15].

A subclass of glass-forming molecular liquids is composed of the network-forming liquids, i.e. liquids with medium range order, as shown by the

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presence of a first peak in the static structure factor (first sharp diffraction peak). It is of great interest to understand whether MCT is able to rationalize also the properties of such liquids, where the mechanisms driving the freezing differ from those occurring in simple liquids. In this paper we analyze molecular dynamics (MD) data for a network forming supercooled liquid, SPC/E water. The simulation consists of a series of trajectories (up to 250 ns) for a system of $N = 216$ rigid molecules interacting through a SPC/E potential with periodic boundary conditions. The details of the simulation are reported in Ref. [12]. In a previous work we discussed the COM self- [12] and collective [13] dynamics of SPC/E water under deep supercooling conditions. We showed that a description of the slow COM motion can be achieved using the prediction of MCT. We showed that, in the temperature range studied, the COM characteristic time, τ (such as, for example, the inverse diffusivity) increases on cooling according to a power law, i.e. $\tau \sim |T - T_c^{\mathrm{MD}}|^{\gamma}$, where T_c^{MD} was found to be around 200 K and $\gamma = 2.7$. In this article, we mainly focus on the relaxation of the angular correlations as a characteristic feature of a molecular liquid. To underline the "universality" of the slowing down processes observed in such a system we perform a comparison between the angular correlators and the self-correlation functions in Section 2. In Section 3 we discuss a possible modification of the COM MCT equations to empirically take into account the coupling between COM and rotational quantities.

2. Rotational dynamics

To investigate the orientational dynamics of water molecules in a supercooled regime we study the time dependent correlation function of the normalized dipole vector, $\vec{\mu}_i$, of the ith molecule, averaged over all the molecules of the system

$$C_1(t) \equiv \frac{1}{N}\left\langle \sum_i \vec{\mu}_i(t) \cdot \vec{\mu}_i(0) \right\rangle = \frac{1}{N}\sum_i \langle \cos\theta_i(t) \rangle, \qquad (1)$$

where $\theta_i(t)$ is the angle between the dipole at time, t, and the same dipole at time $t = 0$. This correlation function corresponds to the average of the first Legendre polynomial $P_1(\cos\theta_i(t))$ and it is the natural generalization of the self-correlation function to the orientational dynamics. In analogy with Eq. (1) the higher order orientational correlators $C_l(t)$ can be defined as

$$C_l(t) \equiv \frac{1}{N}\sum_i \langle P_l(\cos\theta_i(t)) \rangle, \qquad (2)$$

where $P_l(x)$ is the Legendre polynomial of order l. The experimental relevance of these correlation functions is that $C_1(t)$ and $C_2(t)$ can be measured from dielectric measurements and NMR respectively. The set of MD data also allows the calculation of the higher order correlators, which are not accessible in real experiments.

In Fig. 1 plots of the relaxation of $C_1(t)$ and $C_2(t)$ are shown at different temperatures ranging from $T = 285$ to 207 K. We note the presence in the angular correlators of a slow relaxation dynamics which covers a time window of five decades for the higher temperature to eight decades for the lower one. We recover the two step process characteristic of supercooled liquids. An initial (oscillatory) decay to a plateau followed by a slower α-relaxation process. The short time dynamics and the decay to the plateau is almost temperature independent, as well as the magnitude of the plateau. On the contrary the α-relaxation is temperature dependent. The rotational dynamics becomes slower and slower as the temperature is decreased. The longer time relaxation can be properly fitted using a stretched exponential functional form, $A_l e^{-(t/\tau_l)^{\beta_l}}$. τ_l plays the role of a characteristic time for the α-relaxation process.

To underline the fact that the orientational dynamics is coupled to the COM dynamics, we compare in the same figure the orientational correlation function with the COM self-density correlation function at fixed q-vector. At all temperatures, the translational and orientational correlators in the α-region are superimposed, which we suggest shows that decorrelation over distances of the order of q^{-1} is associated with decorrelation over angles of order π/l, l being the order of the Legendre polynomial under scrutiny.

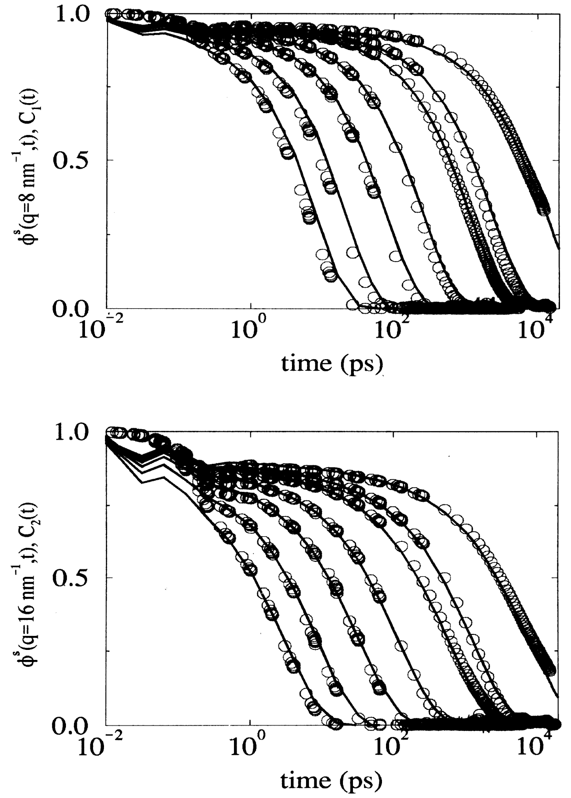

Fig. 1. Time evolution of the angular correlators $C_1(t)$ and $C_2(t)$ as calculated from the MD data (symbols). Curves are plotted at seven different temperatures: $T = 285$, 258, 238, 225, 213, 210, 207 K. Lines are the time evolution of the incoherent density correlators for $q = 8$ and $q = 16\ \mathrm{nm}^{-1}$.

MCT predicts that the correlation times of correlators coupled to the density fluctuations diverge with a power law at the same critical temperature and with the same exponent, γ. From the study of the COM dynamics [12] we found $T_c^{\mathrm{MD}} = (200 \pm 2)$ K and $\gamma = 2.7$.

To compare the scaling of the self-diffusivity and the orientational relaxation times, we plot the COM diffusion coefficient, D, and the rotational relaxation times, τ_l (for several l), raised to the power, $-1/\gamma$, in Fig. 2. All the relaxation times diverge at the same critical temperature, T_c^{MD}, within the numerical error. Moreover the data corresponding to the six lower temperatures agree with the asymptotic power law $\tau_l(T) \propto (T - T_c^{\mathrm{MD}})^{-2.7}$.

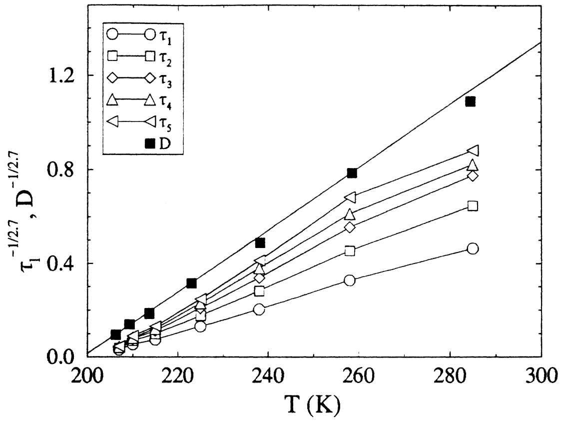

Fig. 2. Comparison between the scaling of the diffusivity with temperature (filled squares) and the scaling of the relaxation times τ_l for different ls (empty symbols). Lines are drawn as guides for the eye.

From the previous discussion and from the comparison in Fig. 2 it appears that translational and rotational relaxations are coupled in the α-relaxation region. Within the cage, molecules have hindered translational and rotational motions. The translational and orientational quantities can relax only in the process of changing local environment, i.e. on the slower time scale of the alpha-relaxation process. This coupling of translational and rotational degrees of freedom is connected to the network structure of water. The ordered structure is mainly due to the formation of strong directional hydrogen bonds which link every molecule to its first neighbors. Thus, the mechanism ruling the glass transition in such a network forming liquid is completely different from that governing the freezing in simple liquids, where the transition is mainly driven by close packing of the molecules. The energetic hydrogen bonds, as compared to the thermal energy, constrain the molecules in “energetic” cages which are responsible for the slowing of the dynamics. The directionality of the bonds couples the translational and rotational motion of the molecules in the process of breaking and reforming the energetic cages. This process implies that a theory describing the process of glass formation in network forming liquids cannot neglect the interplay between translational and orientational degrees of freedom of the molecules.

We now turn to a quantitative analysis of the relaxation of the angular correlators in the α-region. First we show that the time–temperature superposition principle (TTSP) holds for every studied $C_l(t)$. The TTSP, as predicted by MCT, states that curves at different temperatures (but with the same l) fall over the same master curve if the time is rescaled by a l-dependent time scale. To check the TTSP we plot in Fig. 3 $C_1(t/t_1)$ and $C_2(t/t_2)$, where t_l is defined by $C_l(t_l) = 1/e$, i.e. it is the time at which the correlation function decays to a fraction, $1/e$, of its initial value. With this time scaling the curves clearly converge to the same l-dependent master curve. Following the lines of MCT, we then compare, in the time window where the correlators remain close to the plateau, the master curve built up by the envelope of the different curves with the universal master curve of the β-region. The time dependence of the β-correlator is entirely controlled by the exponent b. For the detected $\gamma = 2.7$, MCT predicts a critical exponent $b = 0.5$ which is in agreement with the b obtained by fitting the early coherent and incoherent α-relaxation regions [12,13] to the Von Schweidler law. The universal master curves obtained solving the MCT in the β-region with $b = 0.5$ are represented by the long dashed lines in Fig. 3. As predicted by MCT, the range of validity of the β-correlator is l-dependent [17]. For $l = 2$ we find that the theoretical master curve describes correctly the relaxation in a wide range, in agreement with the result in Ref. [13] for the q-vector corresponding at the pre-peak ($q = 16$ nm^{-1}). For $l = 1$ the time window where the power law holds is smaller and corrections to the Von Schweidler law must be taken into account. The short dashed line in Fig. 3 shows the β-correlator plus the next to leading correction to the power law, t^b, i.e. the t^{2b} order. The introduction of the next order corrections extends the range of validity of the β-master curve by one order of magnitude.

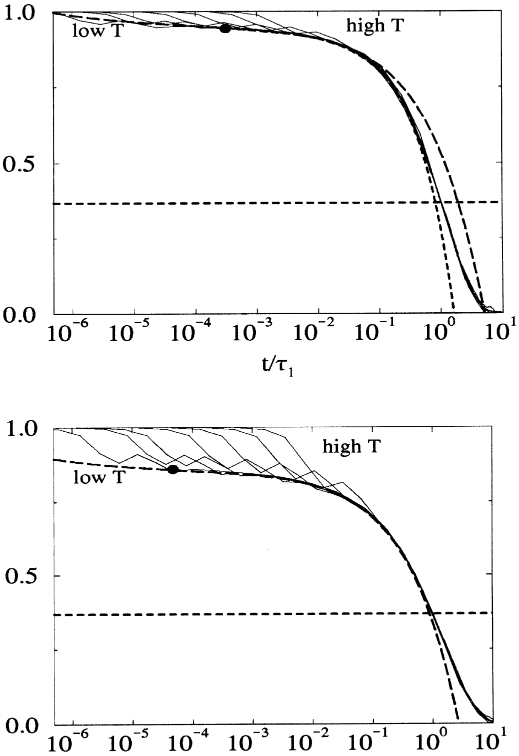

Fig. 3. Time evolution of the angular correlators $C_1(t)$ and $C_2(t)$ as calculated from MD data (solid lines) scaled over the same master curve through a l-dependent scaling of the times. The long dashed lines are the exact solutions of the MCT dynamic equations in the β-region for $\gamma = 2.7$. The black dots indicate the inflection points of the β-correlators in the logarithmic time scale. For $l = 1$ the short dashed line represents the β-correlator plus the next order correction. The long time relaxations can be fitted to a stretched exponential law with $A_1 = 0.94 \pm 0.01$, $\beta_1 = 0.77 \pm 0.05$, $A_2 = 0.84 \pm 0.01$ and $\beta_2 = 0.68 \pm 0.05$. The relaxation times are shown in Fig. 2.

3. A semi-schematic MCT model

The previous analysis provides evidence that MCT is the correct framework for a proper theoretical description of the slowing of the dynamics near the glass transition even for network forming liquids. The MD data presented show that in supercooled SPC/E water the relaxation of the angular correlators, as well as the translational ones, follows the MCT predictions.

The MD data also show that the COM dynamics is coupled with the rotational one, and we do expect that the time evolution of the COM density correlators is affected by the angular correlators. To take into account such a coupling, we propose as a preliminary step toward the investigation of the glass transition in molecular network forming liquids [18], a semi-schematic model for the relaxation of the translational correlation.

The model [18] condenses the interaction between translational and rotational degrees of freedom in a q- and l-independent coupling, χ_R, which increases the strength of the memory function controlling the COM dynamics. We propose to use the usual MCT memory function, $m_q[\phi_q(t)]$ [1], for simple liquids, thus retaining the complete q-dependence of the coherent and incoherent COM density–density correlation functions, multiplied by an effective coupling, χ_R. With the introduction of χ_R we add a further parameter, beside temperature and pressure, which must be tuned to reach the glass transition. If we neglect the effect of the angular correlators on the COM, i.e. $\chi_R = 1$, then the use of usual MCT memory function does not predict a freezing of the dynamics neither at T_c^{MD} nor at any other lower temperature. Indeed, as shown in Fig. 4, if $\chi_R = 1$, the COM correlators decay following the exponential characteristic behavior of high temperature liquids. Increasing the value of χ_R the model predicts a slowing down of the dynamical relaxation, until an ideal glass transition appears for $\chi_R = 1.93$. Thus, by choosing $\chi_R = 1.93$, the model predicts an ideal glass transition exactly at the temperature observed in the simulations.

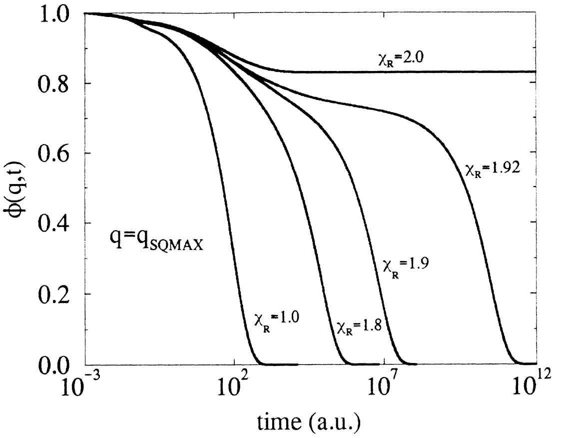

Fig. 4. Time evolution of the density coherent correlator at $q = 18$ nm^{-1} (the position of the maximum of the structure factor) as obtained by solving the semi-schematic MCT equations [18] on a grid of 300 q-vectors. Curves are plotted for different values of χ_R. The numerical structure factor at $T = T_c^{MD}$ has been used in the calculations.

By introducing this simple modification in the MCT, we are able to calculate the complete q-dependence of the static and dynamic quantities ruling the self- and collective COM relaxations. We can solve the equations for the non-ergodicity parameter, the critical amplitudes and the b exponent, and we can calculate the exact time evolution of the correlators. This allows a complete and careful comparison with the numerical data for the COM motion, using as input only the number density, the structure factor at T_c^{MD} and the critical value for χ_R. Fig. 5 shows the non-ergodicity parameter as obtained by fitting the numerical data compared with the theoretical prediction of the semi-schematic model, both for the coherent and incoherent COM correlators. The agreement is striking at low q values, while it becomes worse at large q values, where the dynamics is more sensitive to the detailed geometry of the water molecules. Moreover, the model predicts $b = 0.48$ to be compared with the value $b = 0.5$ calculated from the numerical data. Thus, from the comparison between MD data and the introduced semi-schematic model we learn that, at least in the case under consideration, the interaction of the angular correlators with the COM density fluctuations can be in first approximation

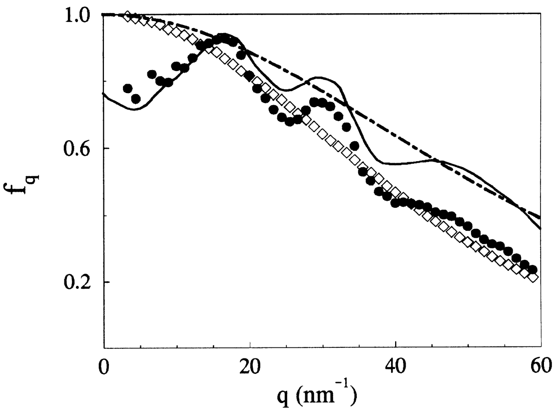

Fig. 5. Comparison between the MD non-ergodicity parameter (symbols) and the semi-schematic model predictions for the self- (squares and dashed line) and collective (circles and solid line) correlation functions.

renormalized in the effective multiplicative constant χ_R.

4. Conclusions

We discuss the possible role of the semi-schematic approach presented here and in Ref. [18], compared to the full MCT description of the rotational translational coupling [14]. The semi-schematic approach requires as only input the COM structure factor, a quantity which can be measured experimentally. Knowing the structure factor, predictions for the q-dependence of the static and dynamic behavior of the COM density fluctuations can be calculated and compared with independent experimental finding. On the other hand, the full MCT solution for non-spherical molecules [14] requires as input several angular static correlators (i.e. the generalization to angular degrees of freedom of the structure factor) which cannot be determined from experiments. In this respect, the semi-schematic model offers an intermediate approach for describing the dynamics of the COM density fluctuations which captures the essential ingredients of the coupling between COM and angular degrees of freedom and which may allow a comparison not only with simulations results but also with experimental data.

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