

Semischematic model for the center-of-mass dynamics in supercooled molecular liquids

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We introduce a semischematic mode-coupling model to describe the slow dynamics in molecular liquids, retaining explicitly only the description of the center-of-mass degrees of freedom. Angular degrees of freedom are condensed in a q -vector independent coupling parameter. We compare the time and q dependence of the density fluctuation correlators with numerical data from a 250-ns-long molecular dynamics simulation. Notwithstanding the choice of a network-forming liquid as a model for comparing theory and simulation, the model describes the main static and dynamic features of the relaxation in a broad q -vector range. [S1063-651X(98)03201-2]

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The slow dynamics in supercooled liquids has recently become a field of increasing interest [1] and a large amount of knowledge has been accumulated from theoretical work [2], experiments [3,4], and simulations [5–7]. It has now become apparent that the ideal mode-coupling theory (MCT) for structural relaxation [2,8] contains the essential ingredients for the description of the molecular dynamics in supercooled states, down to a crossover temperature T_c^{MCT} , where “hopping” processes become dominant [9,10].

Although the MCT was originally developed for simple (atomic) liquids, it appears to be able to rationalize in a coherent way experimental [3,11,12] and numerical simulation results [6,13,14] also for molecular liquids, i.e., for molecules with anisotropic interaction potentials. The lack of theoretical predictions for the behavior of the center-of-mass (COM) and angular degrees of freedom in molecular liquids has been compensated by the use of *schematic models*, where the spectrum of different q vectors and orientations is condensed into one or two representative correlators. The exact solution of these schematic models and the comparison with experiments [11,15] and simulations [16] provide compelling evidence that even molecular liquids can be described in a MCT framework. A full and detailed study assessing the ability of MCT to predict not only the general features of supercooled molecular liquids, but also the q dependence of the COM correlators is highly desirable.

The possibility of describing theoretically the slow dynamics in supercooled molecular liquids is of fundamental importance for assessing the limitations of the ideal MCT, in making contact with experiments, and in tackling the problem of the relation between translational and rotational motions in supercooled states. Theoretical work has recently been undertaken [17–20] in this direction and appears to offer in the future the possibility of a detailed comparison between experiments and theory.

In this article we propose a *semischematic* [21] mode-coupling model to describe the COM dynamics in molecular liquids and we compare the predictions of the model with the COM collective correlation functions, calculated from a long molecular dynamics (MD) simulation for a model of a network-forming molecular liquid [14]. For the first time, the comparison is performed at the highest possible level of de-

tail, i.e., comparing not only static quantities, like the q dependence of the nonergodicity factors, but also the time dependence of the correlators in the entire q range. To our knowledge, such a level of detailed comparison has never been achieved, not even for the simple liquid case. The model we propose is a modification of the MCT equations for simple liquids. It takes into account the coupling between rotational and translational degrees of freedom in a phenomenological way, by introducing a q -independent coupling parameter χ_R that measures the increase in the strength of the memory function $m_q(t)$ induced by the roto-translational coupling. For $\chi_R=1$ we recover the usual MCT equations for simple liquids, while $\chi_R>1$ models a system in which the rotational degrees of freedom slow down the COM dynamics. In contrast to schematic models [2,15] we retain all the q -dependence information for the COM motion [21]. In our MCT model the COM dynamics in the α -relaxation region is entirely controlled by the value of the COM structure factor S_q , by the number density n , and by the value of χ_R . The only T or P dependence in the dynamics arises from the T and P dependence of S_q and n . The intermolecular interaction potential is hidden in the S_q shape.

With the choice for $m_q(t)$ discussed above, the relaxation of the density-density correlation functions $\phi_q(t)$ in the α region [22] is described in terms of a rescaled time $\hat{t} \equiv t/\tau$ [23] by a system of coupled integrodifferential equations:

$$\phi_q(\hat{t}) = m_q(\hat{t}) - \frac{d}{d\hat{t}} \int_0^{\hat{t}} m_q(\hat{t}-s) \phi_q(s) ds, \quad (1)$$

where m_q is

$$m_q[\phi_k(t)] = \frac{\chi_R}{2} \int \frac{d^3k}{(2\pi)^3} V(\vec{q}, \vec{k}) \phi_k(t) \phi_{|\vec{q}-\vec{k}|}(t) \quad (2)$$

and

$$V(\vec{q}, \vec{k}) \equiv S_q S_k S_{|\vec{q}-\vec{k}|} \frac{1}{nq^4} [\vec{q} \cdot \vec{k} (1 - S_k^{-1}) + \vec{q} \cdot (\vec{q} - \vec{k}) \times (1 - S_{|\vec{q}-\vec{k}|}^{-1})]^2. \quad (3)$$

Equations (1) and (3) are the usual MCT expressions while Eq. (2) differs from the one for simple liquids only by the presence of the q -independent multiplicative factor χ_R . In the early α -relaxation region the asymptotic analytic solution of Eq. (1) follows, to leading order, a power law (the von Schweidler law)

$$\phi_q(t) \sim f_q - h_q^{(1)} \left(\frac{t}{\tau}\right)^b + h_q^{(2)} \left(\frac{t}{\tau}\right)^{2b} + O((t/\tau)^{3b}), \quad (4)$$

where f_q , the so-called nonergodicity factor, can be calculated solving the coupled integral equations

$$\frac{f_q}{(1-f_q)} = m_q [f_k]. \quad (5)$$

The exponent b in Eq. (4) is related to the exponent parameter λ by

$$\lambda = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}, \quad (6)$$

where Γ is the Euler gamma function. λ is defined by

$$\lambda \equiv \frac{1}{2} \int_0^\infty dq \int_0^\infty dk \int_0^\infty dp \hat{e}_q^c (1-f_k)^2 e_k^c \frac{\delta^2 m_q}{\delta f_k \delta f_p} (1-f_p)^2 e_p^c, \quad (7)$$

where e^c and \hat{e}^c are the right and left eigenvectors corresponding to the maximum eigenvalue of the stability matrix

$$C_{qk} [f_p] \equiv \left. \frac{\delta m_q [f_p]}{\delta f_k} \right|_{[f_p]} (1-f_k)^2 \quad (8)$$

evaluated at the ideal transition temperature T_c^{MCT} . Details on the calculation of the critical amplitudes $h_q^{(1)}$ and $h_q^{(2)}$ can be found in Ref. [24].

In the late α region it is not possible to solve analytically Eq. (1), but the numerical solution is well fitted by a stretched exponential law (Kohlrausch-William-Watts law)

$$\phi_q(t) \sim A_q^K \exp \left[- \left(\frac{t}{\tau_q^K} \right)^{\beta_q^K} \right], \quad (9)$$

where $\beta_q^K \leq 1$.

We compare the predictions of the semischematic model [Eqs. (1)–(3)] with the corresponding correlators evaluated in a long MD simulation [14]. The simulation was performed using the single point charge/extended (SPC/E) potential [25], a model developed to simulate the behavior of liquid water. It treats the molecule as a rigid unit and models the pair interactions as a sum of electrostatic and Lennard-Jones terms. Previous studies have shown that SPC/E reproduces semiquantitatively the static and dynamic properties of liquid water [25]. In water, an open-structured liquid with an aver-

age coordination number around 4, the slowing down of the dynamics on supercooling is *not* related to packing constraints but it is driven by the formation of a tetrahedral network of strong and highly directional bonds. The role of the cages in reducing the mobility of the molecules is played by the hydrogen bonds that freeze the rotational motion of the molecules and therefore hinder their translational motion. The steric cages that slow down the dynamics in simple liquids are replaced by “energetic” cages.

It has been shown numerically that the SPC/E dynamics in supercooled states is characterized by a two step relaxation process, by a self-similar region in the early α -relaxation region (with a von Schweidler exponent $b = 0.50 \pm 0.05$), and by a stretched exponential decay in the long time α regime. The relaxation times display a power law divergence at the critical temperature $T_c^{\text{MD}} = 200 \pm 2$ K, which has been identified with the ideal MCT transition temperature [14]. Moreover, the rotational correlators follow closely the COM correlators, supporting the view that hydrogen bonds form strong energetic cages and that molecules cannot rotate within a cage. The process of breaking and reforming cages, characteristic of the α -relaxation region is the bottleneck for both COM and rotational diffusion.

We solve numerically Eqs. (1)–(3) on a grid of 300 equispaced q vectors, using as input the COM number density ($n = 32.3 \text{ nm}^{-3}$) and the COM S_q evaluated from the MD data. We study the transition occurring at T_c^{MD} , solving the model for the value of χ_R such that the theoretical T_c^{MCT} coincides with T_c^{MD} . The choice $T_c^{\text{MCT}} = T_c^{\text{MD}}$ leads to $\chi_R = 1.93$ [26].

Since $T_c^{\text{MCT}} = T_c^{\text{MD}}$, we can compare, without other adjustable parameters, results from the MD simulations and theoretical predictions for all q vectors. The comparison [27] for the q dependence of f_q , $h_q^{(1)}$, and $h_q^{(2)}$ in Eq. (4) is shown in Fig. 1 [28]. For reference, we also show S_q , the only q -dependent input in the theory. As in the simple liquid case, the static quantities show oscillations in phase with S_q . We stress, in passing, the peculiar shape of the COM structure factor S_q for SPC/E water when compared to the S_q of simple liquids. The presence of the pre-peak around $q = 18 \text{ nm}^{-1}$ (the analog of the so-called first sharp diffraction peak in silica) is the hallmark of medium range order characteristic of network-forming liquids [29,30].

The agreement between numerical and theoretical values for f_q and $h_q^{(1)}$ is striking although deviations at large q are clearly seen; the difference between theory and simulations for large values of q (i.e., small distances) is not surprising since this is the region where the system is more sensitive to the detailed geometry of the molecules, completely neglected by the model. The agreement for $h_q^{(2)}$ is not as good. We recall that the numerical values for $h_q^{(2)}$ were obtained by a fitting of $\phi_q(t)$ to a second order polynomial in $(t/\tau)^b$ [Eq. (4)] and thus the fitted values are affected by higher order corrections; on the contrary the theoretical $h_q^{(2)}$ is the exact coefficient of the second order term $(t/\tau)^{2b}$.

From the calculated f_q values, we evaluate the exponent parameter λ by numerical integration of Eq. (7). We obtain $\lambda = 0.79$, which yields, through Eq. (6), $b = 0.49$. The value for the exponent b , which controls the self-similar dynamics in the early α region, is in excellent agreement with the one

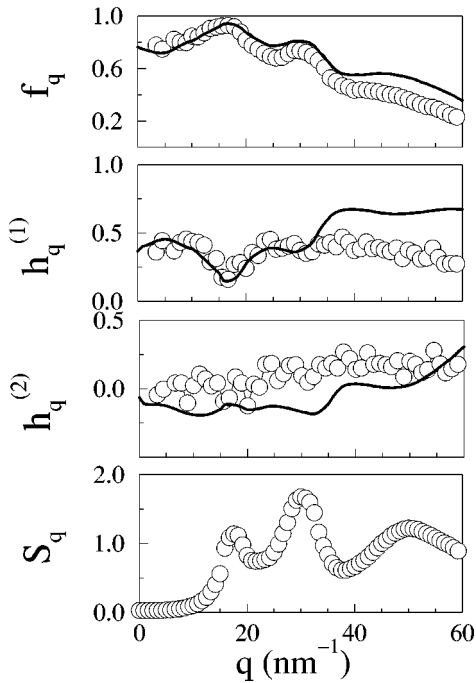


FIG. 1. Comparison between theory (solid lines) and MD simulations (symbols) for the nonergodicity parameter f_q and the critical amplitudes $h_q^{(1)}$ and $h_q^{(2)}$ in Eq. (4). (see Ref. [28]). The center-of-mass structure factor S_q is shown as a reference. MD data are from Ref. [14].

calculated by MD, i.e., $b = 0.50 \pm 0.05$. Thus, the discrepancies between theory and numerical data at large q values do not affect the value of the von Schweidler exponent b . Indeed, the leading contributions to the integral in Eq. (7) come from the maxima of S_q , i.e., from the values at the prepeak and at the main peak, where our model provides the correct results.

To extend the comparison to the late α region, we solve Eq. (1) for all 300 q vectors [31] and we fit, for each q , the time evolution of the MD and theoretical correlators to a Kohlrausch stretched exponential according to Eq. (9). To compare concisely the correlator behavior in the entire q range, we present in Fig. 2 the q dependence of the fit parameters (amplitude A_q^K , relaxation time τ_q^K , and stretching exponent β_q^K). In all cases the quality of the fit is excellent and thus data in Fig. 2 offer a complete comparison of the time evolution of the MD and theoretical correlators in the α region. Again, we find remarkable agreement between the theoretical predictions and the MD data in the low q region, both in the amplitudes and in the relaxation times. Instead, the parameters β_q^K show oscillations in phase with S_q but the theoretical and MD values differ by up to 25%. This indicates that in the MD data, the α -relaxation dynamics covers a larger time range. The differences in β_q^K can be tentatively

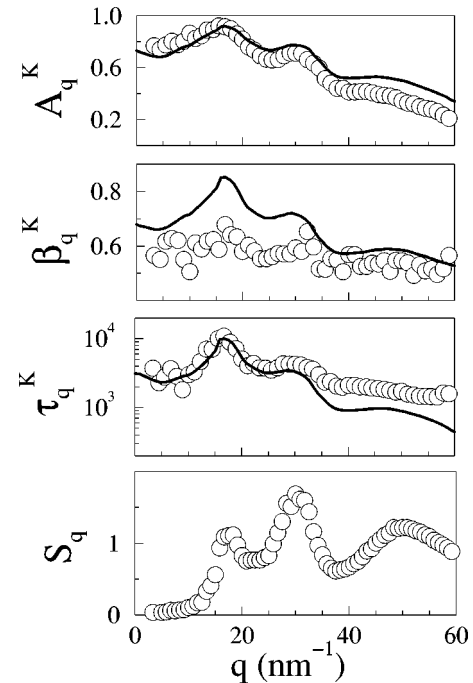


FIG. 2. Fitting parameters to the Kohlrausch-William-Watts law [Eq. (9)] as obtained by the solution of Eq. (1) (solid lines) and by the MD data (symbols). The time scale for the MD values of τ_q^K is 1 ps. In the theoretical values of τ_q^K the time scale has been chosen in an appropriate way as explained in Ref. [28]. MD data are from Ref. [14].

associated with the drastic reduction in the number of coupled correlators retained in the present model, which neglects the angular correlators.

In summary, a simple modification of the MCT equations for simple liquids is able to describe the α -relaxation process in SPC/E water, a model for a molecular network-forming liquid with strong directional bonds. By using as input the fixed value of n and the COM S_q , the theory is able to describe both the q and t dependence of the density-density correlations in a satisfactory way. We stress again that except for the value of χ_R and for a q -independent scaling of time relating \hat{t} with real time [28], no fitting parameters are involved in the comparison. The model can be extended to describe the self-particle dynamics and the collective transverse currents [32].

The approach presented here is a first step towards a full MCT description, which will necessarily include orientational correlations, i.e., the geometry of the molecule [17–20]. Our semischematic approach provides evidence that the slow dynamics in complex molecular liquids can be *quantitatively* described by a very simple modification of the MCT equations for simple liquids, thus retaining the simplicity of the COM description.

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- [22] The time evolution of all correlators in the supercooled regime follows a two-step decay. After the short time microscopic dynamics, the correlators approach a plateau value f_q . The decay after the plateau value is commonly referred to as α relaxation.
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- [28] Due to the scale invariance of the MCT equations for the dynamics in the α -relaxation region [Eq. (1)], the values for the relaxation times τ_q are defined up to a q -independent multiplicative number. This time scale depends on a microscopic characteristic time, which cannot be calculated within the mode-coupling approximations. Therefore we arbitrarily choose the time scale in the comparison between theory and simulations for $h_q^{(1)}$, $h_q^{(2)}$, and τ_q^K .
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