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# Test of the semischematic model for a liquid of linear molecules

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We apply to a liquid of linear molecules the semischematic mode-coupling model, previously introduced to describe the center of mass (COM) slow dynamics of a network-forming molecular liquid. We compare the theoretical predictions and numerical results from a molecular-dynamics simulation, both for the time and the wave-vector dependence of the COM density-density correlation function. We discuss the relationship between the presented analysis and the results from an approximate solution of the equations from molecular mode-coupling theory [R. Schilling and T. Scheidsteger, Phys. Rev. E **56**, 2932 (1997)]. [S1063-651X(98)08311-1]

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## I. INTRODUCTION

The mode-coupling theory (MCT) [1,2] has opened new perspectives in the theoretical understanding of the dynamic slowing down characteristic of supercooled glass-forming liquids [3]. MCT, originally developed to describe the structural relaxation in simple liquids, i.e., in liquids composed by particles interacting via spherically symmetric intermolecular potentials, also offers a coherent picture of the slow dynamics in molecular glass forming liquids, composed of asymmetric molecules. The ability of MCT to model the onset of slow dynamics in molecular liquids has prompted the need to extend the theory to fully take into account the angular degrees of freedom. The extension of MCT to a solute linear molecule in a solvent of spherical particles [4] and to molecular liquids [5,6], which we refer to in the following as molecular MCT (MMCT), has been recently achieved. The center-of-mass (COM) density-density correlation function, which in MCT is the only relevant correlation function, in MMCT becomes coupled to an infinite hierarchy of rotational correlation functions, arising from the expansion of the angular degrees of freedom in spherical harmonics. The MMCT equations for COM and angular correlators have been solved until now for systems of linear molecules under specific approximations [5–7]. Work is currently underway to improve the approximations for dumbbells and to calculate a solution for the general case of molecules of arbitrary shape.

Recently, some of us proposed a parametrization of the role of the rotational degrees of freedom and their effective coupling with the COM density [8]. This approach, which provides a solvable set of coupled equations for the slow dynamics of the COM density-density correlation function, has been named *semischematic* because it retains all the $q$ dependence of the COM correlators but condenses the coupling between COM and angular correlation functions into a single $q$-independent parameter $\chi_R$. A detailed comparison between the theoretical predictions of the model and results from a molecular-dynamics (MD) simulation has been performed for a network forming liquid [8], finding an excellent agreement up to a cutoff $q$-vector value where the microscopic geometric details become dominant.

In the long term, the exact solutions of the MMCT equations are to be preferred because they do not require an *ad hoc* estimate of the translational-rotational coupling and predict also the behavior of the angular correlators. On the other hand, in the short term the semischematic equations are rather appealing because of their simplicity, for the minimal amount of input information required and because the complete time-dependent solution can be achieved with present-day computational facilities. Also, once the ability of the semischematic model to describe the time evolution of the COM correlation functions has been assessed by detailed comparison with MD simulations, comparison with experimental data is foreseeable, again due to the limited need for structural input. For this reason, in this paper we solve the semischematic model for a system of linear dumbbells interacting through a Lennard-Jones (LJ) potential and compare the predictions of the model with the corresponding quantities evaluated from long MD simulations of the same liquid [9]. The choice of a liquid of dumbbells for which the MMCT equations have been previously solved approximately [7] allows at the same time a comparative discussion of the two theoretical methods.

## II. THEORY

The semischematic model is defined by introducing in the ideal MCT equations for simple liquids an effective coupling parameter $\chi_R$ which models the caging effect of the molecular rotational motion on the COM dynamics, i.e., the slowing down of the COM relaxation introduced by the angular degrees of freedom. The resulting system of integrodifferential equations [8] describes the time evolution of the normalized density-density COM correlation functions $\phi_q(t) = S_q(t)/S_q$, $S_q(t)$ being the dynamic structure factor

$$S_q(t) = \frac{1}{N} \langle \rho_q(t)^* \rho_q(0) \rangle \tag{1}$$

and $S_q = S_q(0)$ the static structure factor. The unknown $\chi_R$ is fixed once and for all by requiring that the ideal glass transition temperature in the model $T_c^{\mathrm{MCT}}$ coincides with the temperature calculated from the analysis of experimental or MD data. The imposed equality of the theoretical and MD temperatures is very important because it allows us to compare the numerical and the MD data at the same reference $T$, i.e., with the same structure factor and the same thermal broadening [10]. A larger value of $\chi_R$ corresponds to a stronger slowing down of the COM relaxation due to the interaction with the rotational motion. If $\chi_R = 1$, the semischematic model coincides with the standard MCT [1].

The physics described by the semischematic model is the same as for the ideal MCT. It predicts that when $T < T_c^{\mathrm{MCT}}$, $\phi_q(t)$ does not relax to zero at long times and the COM dynamics is frozen. Above $T_c^{\mathrm{MCT}}$, the correlator $\phi_q(t)$ decays with a typical two-step relaxation process, characterized by the fast decay to a plateau value (the nonergodicity parameter) followed by a slow relaxation to zero ($\alpha$ relaxation) which gets slower and slower as $T_c^{\mathrm{MCT}}$ is approached.

The semischematic model describes the dynamic evolution of $\phi_q(t)$ in the time region where the slow dynamics becomes dominant ($\alpha$ region) by the system of coupled equations,

$$\phi_q(\hat{t}) = m_q(\hat{t}) - \frac{d}{d\hat{t}} \int_0^{\hat{t}} ds\, m_q(\hat{t}-s)\, \phi_q(s), \tag{2}$$

where the time variable $\hat{t}$ is defined in terms of a characteristic time scale which diverges at $T_c^{\mathrm{MCT}}$ [1]. The *memory function* $m_q$ is a quadratic functional of the correlations $\phi_q(t)$ themselves,

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

and its increase on cooling is responsible for the slowing down of the relaxation process. The parameter $\chi_R$ enters in Eq. (3) as a $q$-independent multiplicative factor, thus increasing the strength of the COM memory function.

The vertices in Eq. (3) are defined as

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

and are functions of the COM $S_q$ and inversely proportional to the density.

Note that Eq. (2) ignores the bare transport coefficient as well as the phonon frequencies. Such approximation is motivated by the structure of the MCT equations, which in the vicinity of the critical temperature [1] become scale invariant. In this paper we will compare data calculated from MD simulations with the corresponding theoretical quantities evaluated close to the ideal glass transition temperature, where any information on the bare transport coefficient and on the phonon frequencies drops out. Recently, this theoretical prediction has been subjected to an accurate test in Ref. [11] where it has been shown that the slow dynamics close to $T_c$ is the same for both Newtonian and stochastic microscopic dynamics.

The infinite time limit $f_q$ of $\phi_q(t)$ can be calculated solving self-consistently on a discrete set of $q$ values the coupled integral equations

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

using as input the number density $n$ and $S_q$ which can be calculated from the MD data or measured experimentally.

Having chosen $\chi_R$ properly, at the ideal glass transition temperature the solution $f_q$ of Eq. (5) jumps discontinuously from zero to a nonzero value, which defines the critical nonergodicity parameter $f_q^c$ [1,2]. In what follows, we will neglect the upper index in the nonergodicity parameter.

In the supercooled liquid phase, after the plateau of height $f_q$, $\phi_q(t)$ follows an initial power-law decay (von Schweidler law), ruled by a $q$-independent scaling exponent $b$, followed by a stretched exponential relaxation (Kohlrausch-William-Watts law):

$$\phi_q(t) \sim A_q^K \exp\left[ -\left( \frac{t}{\tau_q^K} \right)^{\beta_q^K} \right]. \tag{6}$$

The range of validity of the von Schweidler law is strongly $q$ dependent [12] and, therefore, it is worthwhile to consider also the second-order corrections:

$$\phi_q(t) \sim f_q - h_q^{(1)} \left( \frac{t}{\tau} \right)^b + h_q^{(2)} \left( \frac{t}{\tau} \right)^{2b} + O((t/\tau)^{3b}). \tag{7}$$

The exponent $b$ can be calculated solving

$$\lambda = \frac{\Gamma(1+b)^2}{\Gamma(1+2b)}, \tag{8}$$

where $\Gamma$ is the Euler gamma function and the *exponent parameter* $\lambda$ is defined by

$$\lambda \equiv \frac{1}{2} \int_0^\infty dq \int_0^\infty dk \int_0^\infty dp\, \hat{e}_q^c (1-f_k)^2 e_k^c \frac{\delta^2 m_q}{\delta f_k \delta f_p} (1-f_p)^2 e_p^c. \tag{9}$$

In Eq. (9), $e^c$ and $\hat{e}^c$ are the right and left eigenvector corresponding to the maximum eigenvalue of the stability matrix

$$C_{qk}^c[f_p] \equiv \frac{\delta m_q[f_p]}{\delta f_k} (1-f_k)^2 \tag{10}$$

evaluated at the critical point. The critical amplitude $h_q^{(1)}$ is

$$h_q^{(1)} = (1-f_q)^2 e_q^c \tag{11}$$

while $h_q^{(2)}$ is calculated theoretically according to the correction formulas to the asymptotic laws reported in Ref. [12].

In Sec. IV we present the solution of the static and dynamic equations reported above for a liquid of linear molecules. Some of us have recently solved the problem of the estimation of the ideal critical temperature and of the calculation of the corresponding nonergodicity parameter for the liquid under investigation solving the MMCT equations within some suitable approximations [6,7]. We thus show in Sec. IV a comparison between the predictions of MMCT for the slow relaxation in a liquid of linear molecules and the corresponding predictions of the semischematic model.

To facilitate the reading of the present paper, we present here a brief outline of the MMCT for linear molecules. We refer the interested reader to Refs. [5–7].

According to MMCT, the relevant variables for the description of the slow dynamics of supercooled molecular glass forming liquids are the generalized correlation functions

$$S^m_{ll'}(q,t)=\frac{1}{N}\,\langle \rho_{lm}(q,t)^*\rho_{l'm}(q,0)\rangle, \qquad (12)$$

where the density functions are defined by

$$\rho_{lm}(\vec{q},t)=i^l\sqrt{4\pi}\sum_{j=1}^{N} e^{i\vec{q}\cdot\vec{x}_j(t)}Y_{lm}(\Omega_j(t)). \qquad (13)$$

In Eq. (13) the sum runs over the $N$ molecules of the liquid, $\vec{x}_j$ is the COM position of the $j$th molecule, and $Y_{lm}(\Omega_j)$ are the spherical harmonics for its Euler's angles. The index $l$ ranges over the whole set of non-negative integer numbers, while $m\in[-l,l]$. For $l=l'=0$ the correlation function defined in Eq. (12) coincides with the COM correlator $S_q$ studied by the usual MCT and the semischematic model. Due to the lack of rotational invariance of the molecules, the correlation functions depend both on modulus and orientation of the wave vector. In Eq. (12) we have chosen a reference frame where $\vec{q}$ points in the direction of the $z$ axes, which offers the advantage of diagonality of the correlators with respect to $m$. The evolution equations for the correlators in Eq. (12) are a generalization of Eq. (2) for a single $q$-dependent correlator. The slowing down of the relaxation is ruled by an infinite set of memory functions $[M^m_{ll'}(q,t)]^{\alpha\alpha'}$ which are quadratic functionals of the whole set of correlators (12). The extra indices $\alpha,\alpha'\in\{T,R\}$ are related to projection operations on the longitudinal translational ($T$) and rotational ($R$) currents. For the aims of this paper we underline that in MMCT the time evolution of each correlator is coupled, through the memory functions, to every other correlator. This means that, due to the dependence of $[M^0_{00}(q,t)]^{TT}$ on both the translational and rotational correlators, the dynamics of the COM correlator $S^0_{00}(q,t)$ is affected by the time evolution of every angular correlation function $S^m_{ll'}(q,t)$ with $l,l'\neq 0$.

With the cutoff $l\leqslant 2$, the nonergodicity parameters $f^m_{ll}(q)=\lim_{t\to\infty}S^m_{ll}(q,t)/S^m_{ll}(q)$ have been calculated for the liquid of LJ dumbbells in the approximation of diagonality in $l$, i.e., $S^m_{ll'}(q,t)\approx\delta_{ll'}S^m_{ll}(q,t)$ and $[M^m_{ll'}(q,t)]^{\alpha\alpha'}\approx\delta_{ll'}[M^m_{ll}(q,t)]^{\alpha\alpha'}$ [7]. We stress that this diagonality was also demanded for the static correlators $S^m_{ll'}(q)$, in order to keep the MMCT equations as simple as possible. The input of the calculations are the number density of molecules and all the diagonal static structure factors $S^m_{ll}(q)$ up to $l=2$ as evaluated from the set of MD data [9].

In this approximation scheme the MMCT equations for the long time limit of the COM and angular correlators can be solved on varying the temperature. The model predicts the existence of a completely ergodic (liquid) phase down to a critical temperature $T_t^{\mathrm{MMCT}}=0.383$ where the COM dynamics runs into a nonergodic (glassy) phase while the angular dynamics is still liquidlike. On lowering the temperature further, a second critical temperature $T_r^{\mathrm{MMCT}}$ appears, characterized by the freezing of both angular and COM dynamics. This splitting of critical temperatures is an artifact of the diagonalization approximation and is not observed when the approximation $l\neq l'$ is waived, at least for the static correlators [13]. Indeed, in the analysis of the MD simulation, rotational and translational critical temperatures coincide, as discussed in Sec. III. This unphysical splitting of the theoretical critical temperatures implies that, for temperatures higher than $T_r^{\mathrm{MMCT}}$, MMCT in the diagonalization approximation is completely equivalent to the ideal MCT for simple liquids, since the angular dynamics does not contribute to the slowing down of the relaxation. For this reason, the theoretical COM critical temperature $T_t^{\mathrm{MMCT}}$ is 25% lower than the numerical critical temperature $T_c^{\mathrm{MD}}$.

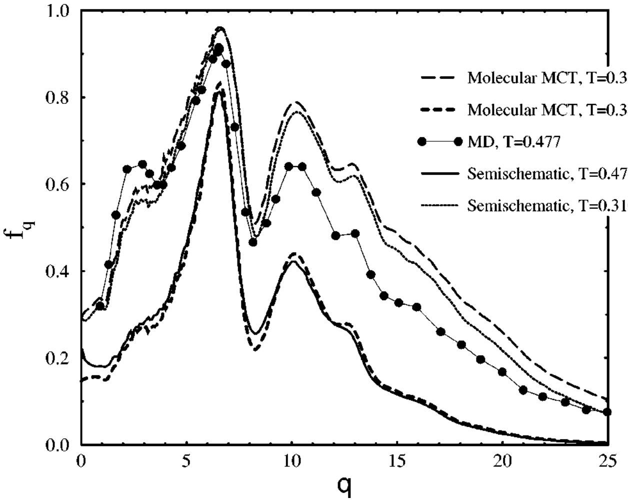

FIG. 1. COM nonergodicity parameter $f_q$ as calculated by solving Eq. (5) (solid line) and as evaluated from the MD simulations [9] (symbols). For comparison also the COM nonergodicity parameters as predicted by MMCT are reported at two different temperatures (dashed lines). The dotted line shows $f_q$ as predicted by the semischematic model at $T=0.310$. The unit of $q$ is $\sigma_{AA}^{-1}$ while the unit of temperature is $\epsilon_{AA}$ (setting $k_B=1$). The MMCT curves are from Ref. [6].

In Fig. 1 we show the results (from Ref. [6]) for the long time limit of the COM correlator $S^0_{00}(q,t)$ (normalized at its $t=0$ value) for the two different critical temperatures (short and long dashed lines). For $T>T_t^{\mathrm{MMCT}}$, the COM correlator decays to zero in a finite time interval (ergodic phase), while at $T_t^{\mathrm{MMCT}}$ its infinite time limit jumps to a nonzero value, namely the nonergodicity parameter $f^0_{00}$. The rotational dynamics is still in a liquid phase, i.e., all the angular correlators vanish in the long time limit until the temperature is lowered down to $T_r^{\mathrm{MMCT}}$. At $T_r^{\mathrm{MMCT}}$, the transition for the angular correlators occurs and the angular dynamics starts to contribute to the nonergodicity parameter. This means that also the angular correlators contribute to the structural arrest of the COM dynamics. From a mathematical point of view, at $T_r^{\rm MMCT}$ the angular correlators start to play a role in the calculation of the COM memory function $[M_{00}^0(q,t)]^{TT}$. The long dashed line in Fig. 1 represents the infinite time limit of the normalized COM correlator. We underline that, at $T_r^{\rm MMCT}$, the COM is in a deep glassy phase and the long time limit of $S_{00}^0(q,t)$ is therefore higher than the critical nonergodicity parameter. All the details of the calculation, both for the angular and COM quantities, can be found in Ref. [6].

## III. MODEL AND SIMULATION DATA

The model under investigation is a one-component system containing $N=500$ rigid diatomic molecules. Each molecule consists of two atoms, labeled $A$ and $B$, separated by a distance $d$. The interaction between two molecules is built up by pair interactions between the atoms, which are due to the LJ potentials,

$$V_{\alpha\beta}(r)=4\epsilon_{\alpha\beta}\left[\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{12}-\left(\frac{\sigma_{\alpha\beta}}{r}\right)^{6}\right],$$

$$\alpha,\beta\in\{A,B\} \tag{14}$$

with LJ parameters $\epsilon_{AA}=\epsilon_{AB}=1.0, \epsilon_{BB}=0.8$ and $\sigma_{AA}=\sigma_{AB}=1.0, \sigma_{BB}=0.95$, i.e., $\epsilon_{AA}$ was chosen as the unit of energy and temperature ($k_B=1$) and $\sigma_{AA}$ as the unit of length. The unit of time is then $[(\sigma_{AA}^2 m)/(48\epsilon_{AA})]^{1/2}$, where $m$ is the mass of an atom which is chosen to be equal for both types of atoms. The slight head-tail asymmetry of the dumbbell assures, together with the choice of $d=0.5$ as interatomic distance, a good coupling between translational and rotational motion on the one hand, and avoids crystallization into a liquid crystalline phase and the intersection of two dumbbells on the other.

After equilibrating the system in the $(N,p,T)$ ensemble for times which exceeded the relaxation times of the system even at the lowest temperature, the production runs were carried out in the microcanonical ensemble. To improve the statistics, the data for each temperature were averaged over at least eight independent runs. Further details about the simulation can be found in Ref. [9], from which we take part of the data to be compared with the theoretical results.

In the frame of MCT, the presence of a critical temperature affects the $T$ dependence of several observables. For example, the Debye-Waller factors are predicted to show a square root singularity at $T_c$. The $\alpha$-relaxation times for all possible correlators coupled with the density fluctuations follow a power law in $|T-T_c|$ on approaching $T_c$ from above. Close to $T_c$, the power law crosses to an activated dynamics law due to the increased relevance of the hopping processes. These behaviors can be used to estimate from the MD data the location of the critical temperature $T_c^{\rm MD}$, as shown, for example, in Refs. [14–16,9,17].

In the present case, the critical temperature for the COM was determined from the simulation by fitting the $\alpha$-relaxation time and the diffusion constant $D$ with power laws

$$\tau\propto(T-T_c^{\rm MD})^{-\gamma}, \quad D\propto(T-T_c^{\rm MD})^{\gamma} \tag{15}$$

and it was found to be $T_c^{\rm MD}=0.477$. The numerical values for the nonergodicity parameter $f_q$, the critical amplitude $h_q^{(1)}$, and the second-order correction $h_q^{(2)}$ at the critical temperature $T^{\rm MD}=0.477$ are also taken from Ref. [9]. They were evaluated by fitting the decay from the plateau in $\phi_q(t)$ with the von Schweidler law Eq. (7), including the second-order correction. From the same procedure the critical exponent $b=0.55$ is also obtained and, via Eq. (8), one gets for the exponent parameter $\lambda$ the result $\lambda=0.76$. Furthermore, we have examined the time dependence of the MD correlator $\phi_q(t)$ in the $\alpha$ region by evaluating the amplitudes $A_q^K$, stretching exponents $\beta_q^K$, and relaxation times $\tau_q^K$ of a Kohlrausch-Williams-Watts fit [Eq. (6)].

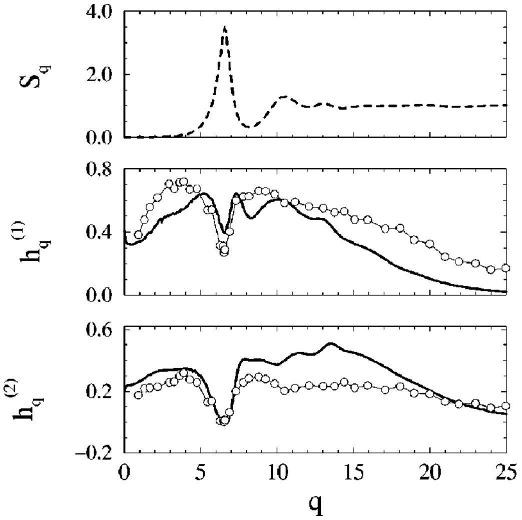

FIG. 2. Critical amplitudes $h_q^{(1)}$ and $h_q^{(2)}$ in the von Schweidler law Eq. (7) as predicted by the semischematic model (solid lines) and as calculated from the MD data (symbols). The static structure factor $S_q$ used as input of the theoretical calculation is also shown. The unit of $q$ is $2\pi\sigma_{AA}^{-1}$.

## IV. RESULTS

We solve for the liquid of LJ dumbbells the semischematic equations introduced in Sec. II using as input for the calculation the static structure factor $S_q$ as obtained from the simulation (Figs. 2 and 3) and the COM number density $n=0.719$ at $T^{\rm MD}=0.477$. We solve Eq. (5) on a grid of 300 equispaced $q$ values extending up to $q\sigma_{AA}=25$. This $q$-vector range covers about four times the position of the first peak in the static $S_q$ and extends up to the region where $S_q$ has practically reached its asymptotic value of 1. Published work on the hard-sphere system [18,12] has shown that the results are not affected by the mesh size if the shape of the structure factor is well resolved and the range extends up to values such that $S_q=1$.

We find that the condition $T_c^{\rm MCT}=T^{\rm MD}$ fixes the value of $\chi_R$ to 1.17, which suggests that the coupling between COM and angular degrees of freedom in LJ dumbbells increases the COM memory function about 20%. If compared to the value $\chi_R=1.93$ found for SPC/E water [8,17], this result highlights the weaker hindering effect of the rotational mo-

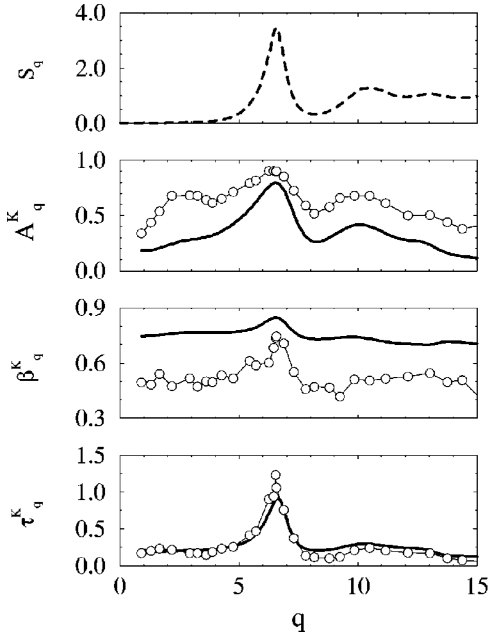

FIG. 3. Amplitude $A^K_q$, stretching exponent $\beta^K_q$, and relaxation time $\tau^K_q$ in the Kohlrausch-William-Watts law Eq. (6). Lines are obtained fitting Eq. (6) to the exact time-dependent solution of Eq. (2) while symbols are evaluated fitting the same law to the MD data. The MD time unit for $\tau^K_q$ is $10^5[(\sigma^2_{AA}m)/(48\epsilon_{AA})]^{1/2}$ while the MCT relaxation times are arbitrarily scaled. The unit of $q$ is $2\pi\sigma^{-1}_{AA}$. The static structure factor is shown as a reference.

tion in a liquid of LJ linear molecules with respect to the strong one observed in a hydrogen-bonded network-forming liquid. In water, the highly energetic hydrogen bonds build up the network structure which is responsible for the caging of the molecules in the glass phase. The motion of the COM of the molecules is completely dependent on the breaking and reforming of the hydrogen bonds, i.e., it is definitely correlated to the angular dynamics.

The solution of Eq. (5) for $\chi_R = 1.17$ as a function of the wave vector $q$ is shown in Fig. 1 together with the COM nonergodicity parameters as calculated from the MD data. The theoretical $f_q$ oscillates in phase with the MD data, but underestimates the amplitude, especially at large $q$ vectors.

Although the phase relation between $f_q$ and $S_q$ may seem at a first glance a trivial effect of using $S_q$ as input in the theory, we stress that the $f_q$ value at wave vector $q$ is controlled by Eq. (2) and thus it is the result of a three-dimensional integration which involves the entire $q$ dependence of $S_q$.

The shoulder around $q = 3$, which may be attributed to the rotational-translational coupling, as the orientational correlator $S^0_{11}(q)$ has a maximum at this $q$, is also underestimated. This notwithstanding, the semischematic $f_q$ captures the $q$ dependence of the nonergodicity parameter as calculated from the MD data.

The simplicity of the semischematic equations allows us to study, besides $f_q$, also the complete time relaxation of $\phi_q(t)$. According to the theoretical predictions outlined in Sec. II, we calculate the critical amplitudes $h^{(1)}_q$ and $h^{(2)}_q$ and the exponent $b$ which rule the early $\alpha$-relaxation behavior [Eq. (7)].

In Fig. 2, we present a comparison between the theoretical predictions of the semischematic model for the critical amplitudes $h^{(1)}_q$ and $h^{(2)}_q$ and the same quantities as calculated by fitting Eq. (7) to the density-density correlation functions, i.e., with a quadratic fit in $t^b$. The fitting coefficients $h^{(1)}_q/\tau^b$ and $h^{(2)}_q/\tau^{2b}$ can be compared with the theoretical critical amplitudes after fixing, once and for all, the $q$-independent time scale $\tau$, introduced by the scale invariance of Eq. (2). The agreement is satisfactory in a wide range of $q$ values. The theoretical value for the exponent parameter, as calculated from Eq. (9), is $\lambda = 0.63$, to be compared with $\lambda = 0.76$ as obtained by the simulation, i.e., the difference between the two is about 15%. This yields a theoretical critical exponent $b = 0.75$, while the exponent calculated from MD data is $b = 0.55$. In the case of SPC/E water, the theoretical and MD values of $b$ coincide within the numerical error. Such a finding is consistent with the remarkable agreement of the nonergodicity parameters over both the relevant peaks of the structure factor.

The comparison between MD data and the prediction of the semischematic model can be extended to the long time region. We solve the complete dynamic set of Eq. (2) in the whole $q$ range [19].

We fit the stretched exponential law [Eq. (6)] to the long time relaxation (late $\alpha$ region) and we compare the obtained amplitude $A^K_q$, relaxation time $\tau^K_q$, and stretching exponent $\beta^K_q$ with the corresponding quantities as calculated by fitting the MD relaxation. The comparison of the complete $q$ dependence of $A^K_q$, $\tau^K_q$, and $\beta^K_q$ is shown in Fig. 3. The theoretical and numerical relaxation times are in perfect agreement. Less satisfactory, as in the case of water, is the theoretical prediction for $\beta^K_q$ for which the theory provides the correct qualitative $q$ dependence, but failing in amplitude up to 30%. The error in the values of the stretching exponents is expected on the basis of the drastic simplification adopted in the semischematic approach, which condensates the coupling between the infinite set of angular correlator and the COM correlator. Indeed, in phenomena in which the decay of correlation results from the sum of several independent relaxation processes, a smaller $\beta$ indicates a wider distribution of relaxation times [20]. As expected, $A^K_q$ has the same behavior as $f_q$ both for theory and simulation.

The choice of the dumbbell liquid is particularly interesting because it allows a comparison between the theoretical predictions of the semischematic model and those of MMCT, which provides a deeper understanding of the basic approximation in the model, i.e., the assumption that the coupling between the COM and angular degrees of freedom can be quantified in a multiplicative $q$-independent factor $\chi_R$. The comparison requires a certain degree of care, because of the difference in the theoretical estimate of $T^{\mathrm{MMCT}}$, rather different from $T^{\mathrm{MD}}_c$. Indeed, while in the case of the semischematic model the MD and the theoretical $f_q$ are evaluated at the same temperature, in the case of MMCT the nonergodicity parameters are calculated using as inputs the structure factors from the simulations *but* evaluated at temperatures different from $T^{\mathrm{MD}}_c$.

Since in the diagonal approximation of MMCT, for $T > T^{\mathrm{MMCT}}_r$ the angular correlators decay to zero, they do not contribute to the structural arrest of the COM dynamics. The

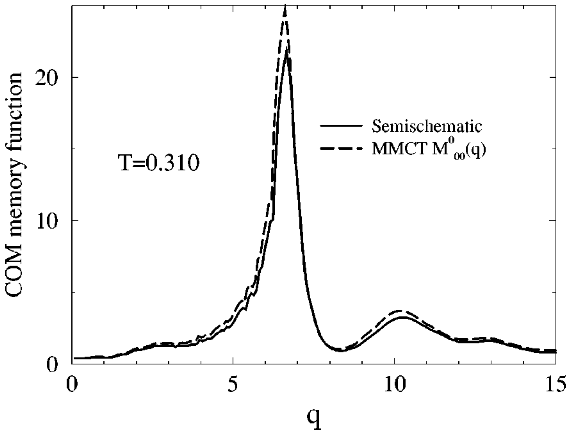

FIG. 4. COM memory function as predicted by the semischematic model Eq. (3) (solid line) and by MMCT (dashed line) at $T_r^{\rm MMCT}=0.310$. The unit of $q$ is $2\pi\sigma_{AA}^{-1}$ while the unit of temperature is $\epsilon_{AA}$ (setting $k_B=1$).

underestimated coupling between translational and rotational degrees of freedom, introduced by the diagonal approximation, is compensated by a decrease of the ideal glass transition temperature from $T_c^{\rm MD}$ to $T_t^{\rm MMCT}$. On the other hand, in the semischematic model, by using the coupling $\chi_R$ as an additional parameter in the theory, it is possible to mimic the role of the angular correlators in increasing the strength of the COM memory function at $T_c^{\rm MD}$ without the need of changing the ideal glass transition temperature. As can be seen from Fig. 1, the two approaches converge to equivalent results for the COM nonergodicity parameter (solid and short dashed lines) but with a considerable difference in the computational times requested.

A better insight into the comparison between the different theoretical approaches can be performed studying the nonergodicity parameter as predicted by the semischematic model at $T_r^{\rm MMCT}$. Keeping fixed once and for all the coupling $\chi_R=1.17$, we can solve Eq. (5) with the memory function Eq. (3). With this choice of temperature the COM dynamics is in a deep glassy phase, both in the semischematic and MMCT descriptions. Thus, being in a nonergodic phase, the COM dynamic structure factor has a finite long-time limit, which is shown in Fig. 1. The semischematic (long dashed line) and MMCT (dotted line) predictions are in perfect agreement. This result can be illustrated by the comparison of the long time limits of the semischematic memory function $m_q$ and the COM MMCT memory function $[M^0_{00}(q)]^{TT}$ at $T_r^{\rm MMCT}$ (Fig. 4). We recall that the angular correlators contribute to $[M^0_{00}(q)]^{TT}$ as well as the COM correlator, while the semischematic $m_q$ is ruled only by the COM $S_q$ and the value of $\chi_R$. Thus, the semischematic model gives rise to the complete functional dependence of the COM memory function on the rotational relaxation in a very simple way, i.e., taking into account only the functional dependence on the COM correlator and summarizing all the remaining coupling in the effective $\chi_R$. This means that the COM dynamics predicted by the semischematic model almost coincides with the corresponding predictions of MMCT in the diagonalization approximation. Furthermore, the model has the advantage that the complete time evolution of the COM correlator can be calculated with current computational resources.

## V. CONCLUSIONS

A theoretical (but relatively simple) description of the COM dynamics in a molecular supercooled liquid is a relevant task which has recently attracted a lot of attention. The situation recalls the early days of the MCT for simple liquids, when the dynamical equations were known but the exact numerical solutions were too difficult to handle. In that situation, simple approximations giving rise to a solvable set of equations were proposed and carefully studied. This class of approximations, which is still extensively used to interpret experimental results in a simple way [21,22], arises from the basic assumption that the $q$ dependence of $S_q$ can be reduced to a single representative $q_0$ vector, i.e., $S_q \propto \delta(q-q_0)$ [23]. In this approximation, which is called the *schematic model*, the $q$ dependence is abandoned in favor of an exact description of one or two representative correlators. In the same spirit, the *semischematic* model provides a method for studying the complete $q$ dependence of the COM dynamics, neglecting the angular degrees of freedom which are condensed in a single $q$-independent parameter $\chi_R$.

Notwithstanding the drastic approximation intrinsic in the proposed approach, we have shown in this paper that the model captures the essential ingredients of the $q$-dependent static and dynamic features of the COM $\alpha$ relaxation. The predicted nonergodicity parameter, relaxation time, and stretching exponent oscillate in phase, the critical amplitudes out of phase, with the COM structure factor, i.e., the model predicts the same qualitative behavior observed in the simulation. The quantitative agreement with the MD data for $f_q$, $h_q^{(1)}$, $h_q^{(2)}$, and $\tau_q$ is satisfactory, especially for $q$ vectors close to the maximum of $S_q$, while the stretching exponent $\beta_K$ is overestimated. This reflects the major weakness of the approach but at the same time clearly indicates the role played by the angular degrees of freedom in controlling the dynamical evolution of the center of mass. If the present observations are discussed together with the semischematic analysis of the dynamics of SPC/E water, a model which mimics a liquid of strong directional hydrogen bonds, it becomes obvious that the value of $\chi_R$ is a measure for the strength of the rototranslational coupling.

The comparison between the semischematic model and the MMCT approximate solutions for the COM nonergodicity parameter and memory function also supports the validity of the assumption of a $q$-independent $\chi_R$. Moreover, the coincidence of the theoretical critical $T$ and the MD one allows for precise comparisons between theory and experiments. Different from the MMCT, the only required input in the model is the COM $S_q$, a quantity which can be experimentally measured by suitably designed neutron or x-ray scattering experiments [24].

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