PHYSICAL REVIEW E VOLUME 60, NUMBER 5 NOVEMBER 1999

Molecular mode-coupling theory for supercooled liquids: Application to water

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(Received 5 May 1999)

We present mode-coupling equations for the description of the slow dynamics observed in supercooled molecular liquids close to the glass transition. The mode-coupling theory (MCT) originally formulated to study the slow relaxation in simple atomic liquids, and then extended to the analysis of liquids composed by linear molecules, is here generalized to systems of arbitrarily shaped, rigid molecules. We compare the predictions of the theory for the *q*-vector dependence of the molecular nonergodicity parameters, calculated by solving numerically the molecular MCT equations in two different approximation schemes, with ''exact'' results calculated from a molecular dynamics simulation of supercooled water. The agreement between theory and simulation data supports the view that MCT succeeds in describing the dynamics of supercooled molecular liquids, even for network forming ones. [S1063-651X(99)06210-8]

PACS number(s): 61.25.Em, 64.70.Pf, 61.43.Fs, 61.20.Ja

I. INTRODUCTION

In recent years, the problem of a detailed theoretical description of the dynamics of *molecular* supercooled liquids has been an area of renewed interest. The success of mode-coupling theory (MCT) [1–6] for simple liquids in describing the weakly supercooled regime has stimulated a considerable amount of work to extend this approach to molecular liquids. Recent contributions include the extension of MCT to describe the rotational dynamics of one linear probe molecule in an atomic liquid [7], the extension of MCT to describe the dynamics — both self and collective — of liquids of linear molecules [8,9], and the MCT extension to treat the dynamics of full molecular systems using a site-site representation [10]. In the first part of this article we report on one further step taken in the description of the dynamics of supercooled molecular liquids, i.e., the extension of MCT to describe the orientational and translational dynamics for liquids composed by rigid molecules of *arbitrary* shape. Within the framework of ''nonlinear fluctuating hydrodynamics'' this has already been achieved by Kawasaki [11]. However, the connection with the *molecular* correlation functions (see below), which are important also from an experimental point of view has not been worked out. This extension will be called *molecular mode coupling theory* (MMCT).

The theoretical predictions formulated in all these approaches, and the proposed approximations are currently under investigation by several research groups. Detailed tests of all these approaches are requested to estimate the quality of the approximations, the predictive power of these different approaches (i.e., the detail of the theoretical descriptions) as well as the limit imposed by the complexity of the MCT equations and the feasibility of their solution. Furthermore, the quality of the approximations may depend on the molecular liquid under investigations, for example on the fragility of the liquid in Angell's classification scheme.

In the second part of this article we present the q dependence of molecular nonergodicity parameters calculated from the MMCT equations for a model system of a supercooled molecular glass-forming liquid. We then compare the theoretical predictions with equivalent quantities calculated from extensive molecular dynamics (MD) simulations. We choose to compare theory and MD results for liquid water. The choice of water as molecular liquid is particularly relevant for testing the quality of the MMCT approach, due to the presence of an extended network of hydrogen bonds and to the peculiar local tetrahedral ordering. The intermolecular water-water interaction is defined by the SPC/E potential [12], which describes the molecule as a rigid planar body and models the pair interactions as a sum of electrostatic and Lennard Jones terms. Due to the partial charges of the atoms, the molecule possesses a dipole moment which is directed along the twofold rotational symmetry axis. When referring to a body-fixed frame of reference for the molecule, we will always choose the direction of the dipole as the z axis. The z axis and the x axis define the plane which is spanned by the molecule.

The test of MCT and MMCT can be done in two different ways. First, one can investigate the validity of some qualitative predictions which are *independent* of the system, i.e., which are the same for both theories. These are, e.g., the power law dependence of the various relaxation times on $T-T_c$, where T_c is the critical temperature for an ideal glass transition, and the universal relationship between the corresponding exponents and their connection with the so-called exponent parameter λ, etc. Second, one may calculate the *numerical* value of, e.g., λ or of the q dependence of the critical nonergodicity parameters, critical amplitudes, etc. Since these quantities depend on the system, one has to use MMCT in the case of molecular liquids. In this first sense, it has been shown in previous papers [13–17] that mode-coupling theory appears to be the correct theoretical framework for the description of the α-relaxation behavior of SPC/E water. Indeed, the results from a MD simulation are satisfactory compared to the predictions of MCT. The comparison has been performed both for center of mass (COM) self- and collective correlators [13–15] and q-independent rotational correlators [16]. Moreover, the *general* predictions of MCT for the q-dependent molecular correlators

$S_{ln,l'n'}(q,m,t)$ have been tested up to $l=2$ in Refs. [17] and [18], finding again a remarkable agreement, both from the qualitative and the semiquantitative point of view. This wide spectra analysis has confirmed the validity of the universality of MCT predictions and has stimulated a deeper, more quantitative understanding of the MCT approach, which we present in this article.

The structure of the article is as follows: In Sec. II we present the complete set of MMCT equations for the slow dynamics in supercooled homogeneous liquids composed by molecules of arbitrary shape. In Sec. III we discuss the two different approximations which we employ to numerically solve the MMCT equations for the general molecule case and discuss some of the numerical techniques used to solve the MMCT equations. Finally, in Sec. IV we solve the equations for the molecular nonergodicity parameters $F_{ln,l'n'}(q,m)$ for SPC/E water and we compare the calculated predictions with the corresponding quantities evaluated from the analysis of the MD trajectories.

II. THEORY

A. Collective correlation functions

We consider a system of N identical, rigid molecules of arbitrary shape described by the center of mass positions $\vec{x}_j(t)$ and the orientations given by the Euler angles $\Omega_j(t) = (\phi_j(t),\theta_j(t),\chi_j(t))$; $j=1,2,\ldots,N$. The microscopic density $\rho(\vec{x},\Omega,t)=\Sigma_j \delta(\vec{x}-\vec{x}_j(t))\,\delta(\Omega,\Omega_j(t))$ in the $6N$-dimensional configuration space is expanded with respect to the complete set of functions given by the plane waves and the Wigner matrices $D^l_{mn}(\Omega)$ [19], to get the tensorial density modes

$$\rho_\kappa(\vec{q},t) \equiv \rho_{lmn}(\vec{q},t) = i^l(2l+1)^{1/2}\sum_{j=1}^{N} e^{i\vec{q}\vec{x}_j(t)} D^{l*}_{mn}(\Omega_j(t)), \tag{1}$$

which are the starting point of a generalized theory. Here, l runs over all positive integers including zero, and m as well as n takes integer values between $-l$ and l. To simplify the notation we often combine l, m, and n in the superindex $\kappa = (l,m,n)$. Our aim is to give a closed set of equations for the matrix **S**:

$$S_{\kappa,\kappa'}(\vec{q},t) = \frac{1}{N}\langle \rho^*_\kappa(\vec{q},t)\rho_{\kappa'}(\vec{q})\rangle \tag{2}$$

of molecular correlation functions. The strategy to derive such equations of motion is the same as was used for atomic liquids and linear molecules and, therefore, explicit calculations shall not be given here. A survey of the MCT formalism for simple liquids can be found in Ref. [1] and detailed calculations for a molecular system can be found in Ref. [8]. We restrict ourselves to pointing out where modifications have to be made in order to treat molecules of arbitrary shape.

In the choice of ''slow variables'' for the projection operator formalism [20,21] one is already forced to make some further considerations. In the MCT for atomic one-component liquids, one uses the density modes $\rho(q)$ and the *longitudinal* current density modes $j(q)$. For molecular liquids this has to be modified. Besides translational degrees of freedom (TDOF), the molecules also possess orientational degrees of freedom (ODOF), and thus we will have to consider two different kinds of current densities. The translational current density modes

$$j^{T\mu}_\kappa(\vec{q},t) = i^l(2l+1)^{1/2}\sum_{j=1}^{N} \dot{x}^\mu_j(t) e^{i\vec{q}\vec{x}_j(t)} D^{l*}_{mn}(\Omega_j(t)), \tag{3}$$

describe the change of the density $\rho_\kappa(\vec{q},t)$ due to translational motion of molecules, while the rotational current modes

$$j^{R\mu}_\kappa(\vec{q},t) = i^l(2l+1)^{1/2}\sum_{j=1}^{N} \omega'^\mu_j(t) e^{i\vec{q}\vec{x}_j(t)} D^{l*}_{m\,n+\mu}(\Omega_j(t)), \tag{4}$$

are responsible for the change of the density due to molecular reorientation. Here, $\vec{\omega}'_j$ denotes the angular velocity in the body-fixed frame. Consequently, $j^{R\mu}_\kappa$ is also a vector in the body-fixed frame. We have skipped the prime because of notational reasons. As in the theory of angular momentum in quantum mechanics, it is more suitable to use spherical components $\mu=0,\pm1$, defined by $a^0=a_z$, $a^{\pm1}=1/\sqrt{2}\,(a_x \pm i a_y)$, instead of the usual cartesian vector components a_x, a_y, a_z. The connection between density and current modes is given by the continuity equation

$$\dot{\rho}_\kappa(\vec{q},t) = \sum_{\alpha=T,R}\sum_{\mu=-1}^{1} q^{\alpha\mu*}_{ln}(\vec{q})\, j^{\alpha\mu}_\kappa(\vec{q},t), \tag{5}$$

with the m-independent coefficients

$$q^{\alpha\mu}_{ln}(\vec{q}) = \begin{cases} \dfrac{1}{\sqrt{2}}(q_x \pm i q_y) & \alpha=T,\mu=\pm1 \\ q_z & \alpha=T,\mu=0 \\ \dfrac{1}{\sqrt{2}}\sqrt{l(l+1)-n(n+\mu)} & \alpha=R,\mu\pm1 \\ n & \alpha=R,\mu=0 \end{cases}. \tag{6}$$

Apart from the separation into translational and rotational currents that was already necessary in the case of the liquid of linear molecules, we will consider *all* components of the currents as slow variables instead of the longitudinal translational currents $j^T_\kappa(\vec{q},t)=(1/q)\Sigma_\mu q^{T\mu*}_{ln}(\vec{q})\, j^{T\mu}_\kappa(\vec{q},t)$, and combined rotational currents $j^R_\kappa(\vec{q},t)=1/\sqrt{l(l+1)}\Sigma_\mu q^{R\mu*}_{ln}(\vec{q}) j^{R\mu}_\kappa(\vec{q},t)$, only.

This increase of the number of relevant variables for the projection operator formalism is enforced by the following considerations. For general molecules possessing three distinct moments of inertia $I_1 \neq I_2 \neq I_3$, it is important to consider the *single* components $j^{R\mu}_\kappa$ as slow variables, instead of j^R_κ from above, because the long time dynamics becomes independent of the moments of inertia only in the first case, which is demanded by experimental observations. It is also sensible to consider the components $j_{\kappa}^{T\mu}$ of the translational currents separately, since the evolution of the density correlators is influenced by dynamic correlations of *all* components of the currents, as can be seen from the following equation:

$$\frac{d^2}{dt^2}\langle \rho_{\kappa}^{*}(\vec{q},t)\rho_{\kappa'}(\vec{q})\rangle = -\sum_{\alpha\alpha'}\sum_{\mu\mu'} q_{ln}^{\alpha\mu}(\vec{q})q_{l'n'}^{\alpha'\mu'*}(\vec{q}) \times\langle j_{\kappa}^{\alpha\mu*}(\vec{q},t)j_{\kappa'}^{\alpha'\mu'}(\vec{q})\rangle, \tag{7}$$

in which the terms $\langle j_{\kappa}^{\alpha\mu*}(\vec{q},t)j_{\kappa'}^{T\pm 1}(\vec{q})\rangle \neq 0$ occur. This dynamic coupling to the transversal currents is induced by the anisotropy of the molecule and exists also in the case of linear molecules.

The projection operator formalism then leads to the following continued fraction for the Laplace transform $\mathbf{S}(\vec{q},z) = i\int_0^{\infty}\mathbf{S}(\vec{q},t)e^{izt}$, $Imz>0$ of the molecular correlation functions:

$$\mathbf{S}(\vec{q},z) = -[z\mathbf{S}^{-1}(\vec{q}) + \mathbf{S}^{-1}(\vec{q})\mathbf{K}(\vec{q},z)\mathbf{S}^{-1}(\vec{q})]^{-1}, \tag{8}$$

$$K_{\kappa,\kappa'}(\vec{q},z) = \sum_{\alpha\alpha'}\sum_{\mu\mu'} q_{ln}^{\alpha\mu}(\vec{q})q_{l'n'}^{\alpha'\mu'*}(\vec{q})k_{\kappa,\kappa'}^{\alpha\mu,\alpha'\mu'}(\vec{q},z), \tag{9}$$

$$\underline{\mathbf{k}}(\vec{q},z) = -[z\underline{\mathbf{J}}^{-1}(\vec{q}) + \underline{\mathbf{J}}^{-1}(\vec{q})\underline{\mathbf{M}}(\vec{q},z)\underline{\mathbf{J}}^{-1}(\vec{q})]^{-1}, \tag{10}$$

where $J_{\kappa,\kappa'}^{\alpha\mu,\alpha'\mu'}(\vec{q},z) = 1/N\langle j_{\kappa}^{\alpha\mu*}(\vec{q})j_{\kappa'}^{\alpha'\mu'}(\vec{q})\rangle$ is the matrix of static current correlations. The reader should note that the underbar of $\mathbf{k}, \mathbf{J}$, and $\underline{\mathbf{M}}$ stands for the additional superscripts $\underline{\alpha\mu}$ and $\underline{\alpha'\mu'}$.

Thus, the derivation of an equation of motion for $\mathbf{S}(\vec{q},t)$ has been reduced to finding an expression for the memory kernel $\underline{\mathbf{M}}(\vec{q},t)$, also called the fluctuating force kernel, since it is the correlation function of a fluctuating force. The approximation scheme of MCT consists of a separation of $\underline{\mathbf{J}}^{-1}(\vec{q})\underline{\mathbf{M}}(\vec{q},t)\underline{\mathbf{J}}^{-1}(\vec{q})$ into a regular part $\underline{\mathbf{m}}^{reg}(\vec{q},t)$, which accounts for the fast motion and the contribution $\underline{\mathbf{m}}(\vec{q},t)$, due to slow pairs of density modes. For an evaluation of $\underline{\mathbf{m}}(\vec{q},t)$, the fluctuating force is projected onto pairs of density modes $\rho_{\kappa_1}(\vec{q}_1)\rho_{\kappa_2}(\vec{q}_2)$. This projection, which introduces the first approximation, leads to a *time-dependent* four-point correlator and a vertex function which involves *static* two-, three- and four-point correlators. In a second approximation, both four-point correlators, static and dynamic ones, are factorized into a product of two-point correlators. In a final step, one can approximate the static three-point correlator by use of the generalized convolution approximation which is easily generalized from linear [8] to arbitrary molecules. As already pointed out above, we will not give the complete derivation here since it is rather involved and analogous to the case of linear molecules. The result for $\underline{\mathbf{m}}(\vec{q},t)$ can be expressed as follows:

$$m_{\kappa,\kappa'}^{\alpha\mu,\alpha'\mu'}(\vec{q},t) = \frac{1}{2N}\left(\frac{\rho_0}{8\pi^2}\right)^2 {\sum_{\vec{q}_1,\vec{q}_2}}' \sum_{\kappa_1,\kappa_1'}\sum_{\kappa_2,\kappa_2'} v_{\kappa\kappa_1\kappa_2}^{\alpha\mu}(\vec{q},\vec{q}_1,\vec{q}_2)\, v_{\kappa'\kappa_1'\kappa_2'}^{\alpha'\mu'*}(\vec{q},\vec{q}_1,\vec{q}_2)S_{\kappa_1,\kappa_1'}(\vec{q}_1,t)S_{\kappa_2,\kappa_2'}(\vec{q}_2,t). \tag{11}$$

Here, the prime denotes summation such that $\vec{q}_1+\vec{q}_2=\vec{q}$. Besides the time-dependent molecular correlators, the number density $\rho_0=N/V$ and the vertex functions appear, which are products of

$$v_{\kappa\kappa_1\kappa_2}^{\alpha\mu}(\vec{q},\vec{q}_1,\vec{q}_2) = \sum_{\kappa_3} u_{\kappa\kappa_3\kappa_2}^{\alpha\mu}(\vec{q},\vec{q}_1,\vec{q}_2)c_{\kappa_3,\kappa_1}(\vec{q}_1) + (1\leftrightarrow 2), \tag{12}$$

where $\mathbf{c}(\vec{q})$ denotes the matrix of direct correlation functions, which is related to the static structure factors by

$$\mathbf{c}(\vec{q}) = \frac{8\pi^2}{\rho_0}(1-\mathbf{S}^{-1}(\vec{q})). \tag{13}$$

The coefficients u are given by

$$u_{\kappa\kappa_1\kappa_2}^{\alpha\mu}(\vec{q},\vec{q}_1,\vec{q}_2) = i^{l_1+l_2-l}\left(\frac{(2l_1+1)(2l_2+1)}{2l+1}\right)^{1/2} \times\mathcal{C}(l_1l_2l;m_1m_2m)q_{l_1n_1}^{\alpha\mu*}(\vec{q}_1) \times\begin{cases}\mathcal{C}(l_1l_2l;n_1n_2n) & \alpha=T\\ \mathcal{C}(l_1l_2l;n_1+\mu\, n_2\, n+\mu) & \alpha=R,\end{cases} \tag{14}$$

and $\mathcal{C}(l_1l_2l;m_1m_2m)$ denotes the usual Clebsch–Gordan coefficients [19].

Equations (8)–(10), together with Eq. (11), form a closed set of equations for the correlation matrix $\mathbf{S}(\vec{q},t)$. The vertex functions given by Eqs. (12)–(14) are determined by the number density ρ_0 and the static structure factors $\mathbf{S}(\vec{q})$, only.

B. Tagged particle correlation function

We will now examine the motion of a *single* molecule that is immersed in a molecular liquid. Again we have a liquid of $N-1$ identical, rigid molecules of mass M and moments of inertia I_1, I_2, I_3, whose center of mass coordinates are denoted as $x_j(t)$, and whose orientations are given by the Euler angles $\Omega_j(t)$. In addition we have, as the *N*th particle, a molecule of mass M' and moments of inertia I_1', I_2', I_3'. As a special case we get the self-correlator of a selected particle within a homogeneous liquid if the tagged particle is identical to the molecules of the surrounding liquid.

Besides the quantities we have already introduced in the previous subsection, we have to consider the density modes for the tagged particle:

$$\rho_\kappa^{(s)}(\vec{q},t) = e^{i\vec{q}\vec{x}_N(t)} D_{mn}^{l*}(\Omega_N(t)), \tag{15}$$

and the corresponding tagged particle correlation function:

$$S_{\kappa,\kappa'}^{(s)}(\vec{q},t) = \langle \rho_\kappa^{(s)*}(\vec{q},t) \rho_{\kappa'}^{(s)}(\vec{q}) \rangle. \tag{16}$$

The slow variables for the projection operator formalism are given by the density modes (15) and the current densities

$$j_\kappa^{(s)T\mu}(\vec{q},t) = \dot{x}_N^\mu(t) e^{i\vec{q}\vec{x}_N(t)} D_{mn}^{l*}(\Omega_N(t)), \tag{17}$$

$$j_\kappa^{(s)R\mu}(\vec{q},t) = \omega'^{\mu}_N(t) e^{i\vec{q}\vec{x}_N(t)} D_{m\,n+\mu}^{l*}(\Omega_N(t)), \tag{18}$$

of the tagged particle. In this case it is necessary to use all components of the rotational currents separately to avoid inertia effects in the long-time behavior. The results of the projection operator formalism are analogous to the equations for the coherent correlations. As a further simplification the static self-correlations are given by $S_{\kappa,\kappa'}^{(s)}(\vec{q}) = \delta_{\kappa,\kappa'}$. Thus, we get

$$\mathbf{S}^{(s)}(\vec{q},z) = -[z\mathbf{1} + \mathbf{K}^{(s)}(\vec{q},z)]^{-1}, \tag{19}$$

$$K_{\kappa,\kappa'}^{(s)}(\vec{q},z) = \sum_{\alpha\alpha'} \sum_{\mu\mu'} q_{ln}^{\alpha\mu}(\vec{q}) q_{l'n'}^{\alpha'\mu'*}(\vec{q}) k_{\kappa,\kappa'}^{(s)\alpha\mu,\alpha'\mu'}(\vec{q},z), \tag{20}$$

$$\underline{\mathbf{k}}^{(s)}(\vec{q},z) = -[z\underline{\mathbf{J}}^{(s)^{-1}}(\vec{q}) + \underline{\mathbf{J}}^{(s)^{-1}}(\vec{q}) \underline{\mathbf{M}}^{(s)}(\vec{q},z) \underline{\mathbf{J}}^{(s)^{-1}}(\vec{q})]^{-1}, \tag{21}$$

with the same coefficients $q_{ln}^{\alpha\mu}(\vec{q})$ as above.

The correlations of the tagged particle will be controlled by the coherent correlations. Therefore, in the mode-coupling approximation for the memory function $\mathbf{m}^{(s)}(\vec{q},t)$, the slow part of $\mathbf{J}^{(s)^{-1}}(\vec{q})\mathbf{M}^{(s)}(\vec{q},t)\mathbf{J}^{(s)^{-1}}(\vec{q})$, the fluctuating forces are projected onto bilinear products of tagged particle and coherent density modes. In the thermodynamic limit, the effect of the tagged particle on the surrounding liquid can be neglected and the coherent correlator is identical to the correlation function for the homogeneous liquid. The mode coupling approximation for the four-point correlation functions thus leads to the following expression for the memory function

$$m_{\kappa,\kappa'}^{(s)\alpha\mu,\alpha'\mu'}(\vec{q},t) = \left(\frac{\rho_0}{8\pi^2}\right)^2 \frac{1}{N} \sum_{\vec{q}_1,\vec{q}_2}{}' \sum_{\kappa_1,\kappa_1'} \sum_{\kappa_2,\kappa_2'} v_{\kappa\kappa_1\kappa_2}^{(s)\alpha\mu}(\vec{q},\vec{q}_1,\vec{q}_2) v_{\kappa'\kappa_1'\kappa_2'}^{(s)\alpha'\mu'*}(\vec{q},\vec{q}_1,\vec{q}_2) S_{\kappa_1,\kappa_1'}^{(s)}(\vec{q}_1,t) S_{\kappa_2,\kappa_2'}(\vec{q}_2,t), \tag{22}$$

with the vertex functions

$$v_{\kappa\kappa_1\kappa_2}^{(s)\alpha\mu}(\vec{q},\vec{q}_1,\vec{q}_2) = \sum_{\kappa_3} u_{\kappa\kappa_3\kappa_1}^{\alpha\mu}(\vec{q},\vec{q}_2,\vec{q}_1) c_{\kappa_3,\kappa_2}^{(s)}(\vec{q}_2). \tag{23}$$

The coefficients *u* are the same as given above and the direct correlation function that describes the interaction between the tagged particle and the surrounding liquid is defined by

$$\rho_0 (c^{(s)}(\vec{q}) \mathbf{S}(\vec{q}))_{\kappa,\kappa'} = \langle \rho_\kappa^{(s)*}(\vec{q}) \rho_{\kappa'}(\vec{q}) \rangle - \delta_{\kappa,\kappa'}. \tag{24}$$

In the special case in which the tagged particle has the same properties as the molecules of the liquid, $\mathbf{c}^{(s)}(\vec{q})$ is just the ordinary direct correlation function of the homogeneous liquid.

Detailed investigations for the tagged particle correlators have been done for a dumbbell molecule in a simple isotropic liquid [7]. The equations given here are the generalization of this theory (for a linear molecule in a simple liquid) to the general case of an arbitrary shaped molecule in a molecular liquid.

III. APPROXIMATIONS

The aim of our numerical investigations was to examine the long-time behavior of the solutions of the equations of motion presented in Sec. II A, i.e., to calculate the critical nonergodicity parameters $\mathbf{F}(\vec{q}) = \lim_{t\to\infty} \mathbf{S}(\vec{q},t)$ and the transition temperature T_c. As input for these calculations we have determined the static structure factors $\mathbf{S}(\vec{q})$ from a MD simulation, as described in detail in a previous publication [17]. As discussed there, the C_{2v} symmetry of the water molecule leads to the consequence that the distinct part $\mathbf{S}^{(d)}(\vec{q})$ of the structure factors vanishes for *n* and/or n' odd, i.e., $S_{lmn,l'm'n'}(\vec{q})$ with *n* and n' odd, only contains information about the self-correlation of the molecules. These symmetry relations allow for a simplification of the equations. As shown in Appendix A, the matrix equation splits into two parts. The matrix elements $S_{lmn,l'm'n'}(\vec{q},t)$ with *n* and n' even, are determined by a closed set of equations which is independent of the correlators with *n* and/or n' odd. The remaining part of the equations, i.e., for *n* and n' odd, is identical to the corresponding tagged particle equations for the self-correlators as presented in Sec. II B.

For these numerical studies, it is further useful to transform the equations to the q-frame representation, i.e., to choose the z axis of the laboratory frame in the direction of the vector $\vec{q}$. The resulting set of equations and some details of their derivation are given in Appendix B. The q frame offers the advantage of the correlation matrices depending only on the modulus $q=|\vec{q}|$, and in addition are diagonal with respect to the indices m and m'. Thus we have to solve self-consistently a set of equations for the nonergodicity parameters $F_{ln,l'n'}(q,m) \equiv F_{lmn,l'mn'}(q\hat{e}_z)$.

The main computational problem in solving the equations for the glass-form factor is the calculation of the memory matrix $m_{\kappa,\kappa'}^{\alpha\mu,\alpha'\mu'}(q)$, due to the enormous number of terms in the summation of Eq. (11). Of course, any attempt at numerical calculation requires the introduction of an upper cutoff l_{co} in l,l', in order to have a finite number of coupled equations. The stable solution $\mathbf{F}(q,m)$ is found as the fixed point of the iterative solution of the given equations.

It has been estimated in several MCT calculations that, in order to have a reasonable convergence towards the fixed point, it is necessary to perform several hundreds of iterations. Although it is possible to considerably reduce the number of elements in the sum of Eq. (11) by taking into account the symmetries of the molecule, a full solution for $l_{co}=2$ is still not feasible.

As discussed in Sec. II, it is necessary to take into account the components of the rotational currents $j^{R\mu}$ separately to avoid inertia effects in the long-time behavior. Thus we have taken into account all corresponding memory functions. With respect to the translational currents, we have decided to take into account only the longitudinal components j^{T0}, i.e., all memory functions with $\alpha=T,\mu=\pm 1$ or $\alpha'=T,\mu'=\pm 1$ are neglected.

The structure of the MMCT equations further offers the possibility of several approximation schemes, differing in the choice of the molecular static structure factors which are taken into account. In this article we present MMCT calculations for two different approximations, which bring the numerical calculations to the frontier of the present computer facilities. In both approximations we neglect the third angular index n in the static quantities, i.e., we include as input of the calculation only the static structure factors $S_{l0,l'0}(q,m)$ and, thus, the direct correlation functions $c_{l0,l'0}(q,m)$. In addition, we put $F_{ln,l'n'}(q,m)$ at zero for n and n' different from zero. This approximation is reflected in the reduction of the number of independent memory kernels to be calculated.

We have examined the intensity and the temperature dependence of the static correlation functions, and we have given some justification for this approximation in a previous publication [17]. Still it has to be noted that it is mainly motivated by the need to reduce the computational burden and we plan to put a significant effort in the direction of a full solution of the MMCT equations, including also the angular index n.

In Ref. [17], it has been shown that the distinct part of the structure factors vanishes for odd n and/or n'. Thus, with $l \leqslant 2$, the approximation $n=n'=0$ essentially means neglecting the coupling with the correlators with $|n|=2$ and/or $|n'|=2$. This approximation is equivalent to neglecting the third Euler angle χ, i.e., the rotations of the water molecules around the dipolar axes. This means that the motion of the water molecules is reduced to the motion of their dipole moments. Thus, we will refer to this first simplification as the *dipole approximation*.

An even stronger approximation is defined by assuming, in addition, that both the static structure factors, the critical nonergodicity parameters, and the memory functions are diagonal in l and l', i.e.,

$$S_{l0,l'0}(q,m)=S_{l0,l0}(q,m)\,\delta_{ll'}, \tag{25}$$

$$F_{l0,l'0}(q,m)=F_{l0,l0}(q,m)\,\delta_{ll'}, \tag{26}$$

$$m_{lm0,l'm'0'}^{\alpha\mu,\alpha'\mu'}(q)=m_{lm0,lm'0'}^{\alpha\mu,\alpha'\mu'}(q)\,\delta_{ll'}. \tag{27}$$

Thus $\mathbf{S}(q,m)$ becomes a diagonal matrix with six nonvanishing elements (the diagonal ones), while $\mathbf{m}(q)$ is still nondiagonal with respect to $\alpha\mu$ and $\alpha'\mu'$. This approximation and also the even stronger restriction of additional diagonality of the memory kernel with respect to $\alpha\mu$ has also been used in the study of a dumbbell in a simple liquid [7], and a liquid of diatomic molecules [22].

We have iteratively solved the equations for the nonergodicity parameters on a grid of 100 q vectors ranging up to 110 nm^{-1}. Within the diagonal approximation, one iteration step requires about 15 minutes on one α station. The dipole approximation requires about two hours of CPU time, and we estimated that a full solution of the MMCT equations including n would require about 4 days per iteration.

IV. RESULTS

We have found $T_c^{MMCT}=206$ K in the diagonal-dipole approximation. At this temperature, the solution of the nonergodicity parameter equations has been iterated until the average difference over the whole q range between the $(n+1)$th iteration $\mathbf{F}^{(n+1)}(q,m)$ and the nth $\mathbf{F}^{(n)}(q,m)$ was of order 10^{-10}. Since the MCT approach to, e.g., a hard sphere system [23], binary liquids [24], and diatomic molecules [25] has shown that MCT overestimates the freezing into a glassy state, we consider fortuitous the agreement between the estimated T_c^{MMCT} and the numerical estimate of the critical temperature from the analysis of the molecular dynamics data, $T_c^{MD}=200\pm 3$ K, for SPC/E water. We want to highlight that despite the diagonalization approximation, in contrast to what has been found for the liquid of Lennard-Jones dumbbells described in Ref. [22], in the case of water the theory does not yield an unphysical splitting of rotational and translational transition temperatures, i.e., all the elements of the theoretical nonergodicity matrix $\mathbf{F}(q,m)$ simultaneously jump from zero to a nonzero value at the same temperature, or in other words: *all* degrees of freedom freeze at a *single* temperature.

In the dipole approximation, i.e., relaxing the diagonality approximation, the equations for $\mathbf{F}(q,m)$ have been solved in a similar way. In this approximation the value of the *critical* $\mathbf{F}(q,m)$ was evaluated, stopping the iterative calculation when the average difference between two consecutive iterations was of order 10^{-8}. In the dipole approximation, the theoretical critical temperature has been found to be about

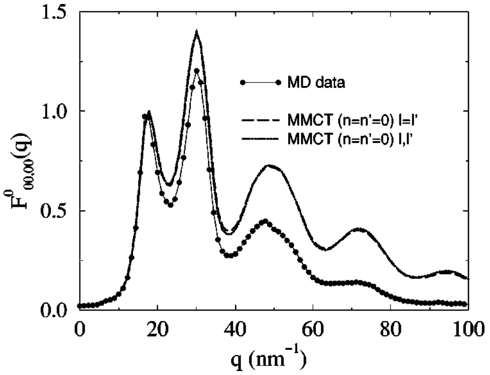

FIG. 1. Critical center of mass nonergodicity parameter $F_{00,00}(q,m=0)$ as calculated from the MD simulation (symbols) compared with the theoretical predictions obtained in two different approximation schemes: MMCT in the diagonal-dipole approximation (dashed line) and MMCT in the pure dipole approximation (dotted line).

$T'^{MMCT}_c=208$ K, which is not so different from T^{MMCT}_c in the diagonal approximation or from the numerical one. As discussed in Ref. [17], it is reasonable to suppose that the transition is driven by the diagonal structure factors, especially the ones with $l=0$ or $l=2$, which are the most sensitive to variations of temperature. It is thus not surprising to observe that the critical temperature is almost insensitive to the introduction of the off-diagonal terms, which display a weaker dependence on *T*.

The theoretical predictions for $\mathbf{F}(q,m)$, in the different approximation schemes, are shown in Figs. 1, 2, 3, and 4, in comparison to the corresponding quantities as evaluated from the MD simulation, fitting the time evolution of the correlators in the early α region to the von Schweidler law [17]:

$$S_{ln,l'n'}(q,m,t)-F_{ln,l'n'}(q,m) \cong -H^{(1)}_{ln,l'n'}(q,m)\hat{t}^{b}+H^{(2)}_{ln,l'n'}(q,m)\hat{t}^{2b}+O(\hat{t}^{3b}). \tag{28}$$

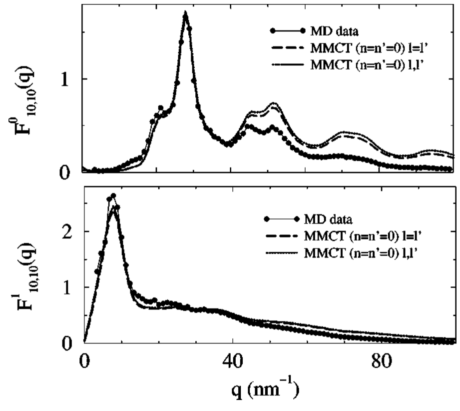

FIG. 2. Diagonal critical nonergodicity parameters with $l=l'=1$ $[F_{10,10}(q,m)]$ as calculated from the MD simulation (symbols) compared with the theoretical predictions of MMCT in the diagonal-dipole approximation (dashed line) and MMCT in the pure dipole approximation (dotted line).

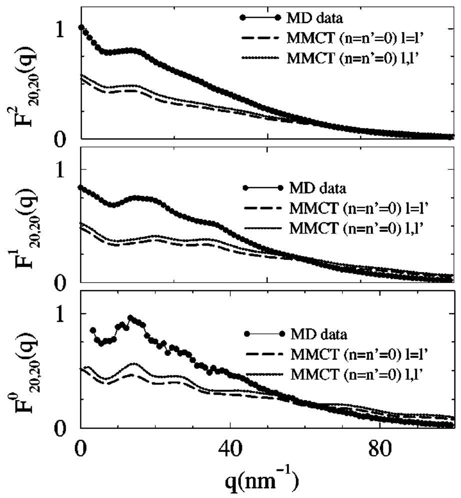

FIG. 3. Diagonal critical nonergodicity parameters with $l=l'=2$ $[F_{20,20}(q,m)]$ as calculated from the MD simulation (symbols) compared with the theoretical predictions of MMCT in the diagonal-dipole approximation (dashed line) and MMCT in the pure dipole approximation (dotted line)

In Fig. 1, the theoretical predictions for the COM nonergodicity parameter in the two approximations examined in this article are compared to the MD data. Both approximations are excellent in the low *q* range (up to around 30 nm^{-1}). The MMCT approximations allow the calculation, beside the COM nonergodicity parameter, also of the angular nonergodicity parameters. Of course, in the diagonal-dipole approximation, only the diagonal elements $F_{l0,l0}$ of the nonergodicity matrix $\mathbf{F}$ can be evaluated. The results are shown in Figs. 2 and 3 together with the predictions for the same quantities as evaluated relaxing the diagonality approximation. The agreement with the numerical data (symbols in the figures) is satisfactory for the $l=1$ nonergodicity parameters (both for $m=0$ and $m=1$), while the predictions corresponding to $l=2$ are less satisfactory. It is reasonable to expect that the worse results obtained for $l=2$ are due to the

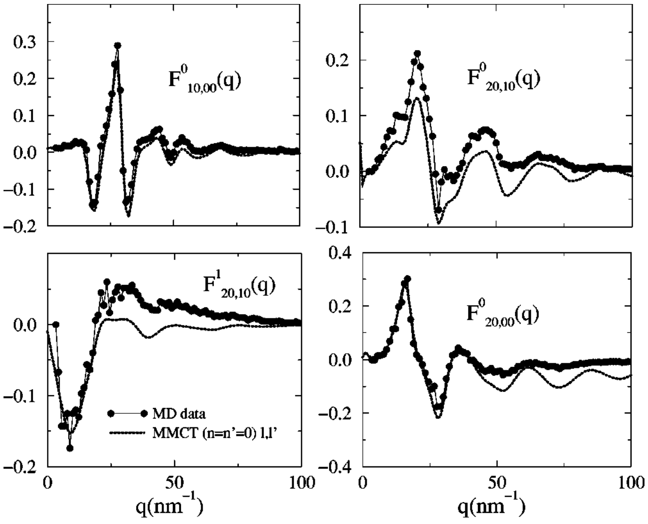

FIG. 4. Off-diagonal critical nonergodicity parameters ($l\neq l'$) as calculated from the MD simulation (symbols) compared with the theoretical predictions of MMCT in the pure dipole approximation (dotted line).

fact that this is exactly the cut-off value, and it is thus more sensitive to ''boundary'' effects. The comparison between theoretical predictions and MD data for the off-diagonal terms of **F**, a comparison which is possible to perform only in the dipole approximation scheme, is shown in Fig. 4. Again, the agreement between MD data and theoretical results becomes worse on increasing l towards l_{co}. By comparing the results for the two different approximations, we note that for both the COM (Fig. 1) and angular (Figs. 2 and 3) nonergodicity parameters, the coupling to the nondiagonal correlators introduced in the pure dipole approximation contribute very little to the determination of the diagonal terms of the glass-form factor. This result, as well as the small variation of the critical temperature within the two approximations, is due to the small amplitudes of the off-diagonal terms with respect to the diagonal ones, and supports the idea that the critical behavior of the system is mainly driven by the more intense structure factors. This consideration suggests the use of only the strongest $S_{ln,l'n'}(q,m)$ as input for the calculation, which may allow the choice of higher values for the cut-off l_{co}.

V. SUMMARY AND CONCLUSIONS

In the present paper we have performed a quantitative test of MMCT for the SPC/E model for water in the supercooled regime. MMCT is an extension of mode-coupling theory for simple liquids to molecular systems. It provides equations of motion for the molecular correlators $S_{\kappa,\kappa'}(\vec{q},t)$ which form a *complete* set for any time–dependent two-point correlator. Of course, there are an infinite number of them, which forces the truncation of the set of MMCT equations at a cut-off value l_{co} for l and l'. In our case, we have chosen $l_{co}=2$. From a pragmatic point of view, this may be justified by the fact that up to today there seems to be no experimental method which allows for the determination of those correlators for l and l' at larger than two, although this can be done for any numerical simulation. Instead of using the molecular correlators, one also could use correlators in a *site-site* representation [20]. MCT for molecular systems in a site-site description has recently been worked out [10]. This type of approach has the advantage that for molecules with a few atoms, the number of correlators is small, e.g., for water there are six correlators at maximum, where one has to take into account that both protons can be distinguished for a classical system. A site–site description, however, has the disadvantage that it is incomplete, i.e., information has been lost. For instance, light scattering, dielectric spectroscopy, NMR, ESR, etc., directly yield *molecular* correlators. Whereas the site-site correlators can be represented by the molecular ones, the reverse is not possible [26]. Hence, from a site-site description, no *exact* information can be deduced for the experimental techniques mentioned above. Nevertheless, it would be worthwhile to solve the molecular MCT equations in the site-site representation, e.g., for water, in order to compare the critical temperature T_c, the critical nonergodicity parameters, etc., with the corresponding quantities from MMCT.

Despite the cutoff for l and l' the MMCT equations are still rather involved. Therefore we decided to perform as a first step, a further approximation, which is that n and n' are put at zero for the static correlators and the nonergodicity parameters. Because of this approximation, we neglect rotations of both protons around the molecular symmetry axis. Within these approximations, we have calculated the (unnormalized) critical nonergodicity parameters $F_{l0,l'0}(q,m)$ in the q frame by solving the corresponding MMCT equations. As we have found that the *diagonal*, *static* correlators $S_{l0,l'0}(q,m)$, compared with the nondiagonal ones, are most dominant with respect to their intensity and temperature dependence [17], we have additionally solved the MMCT equations by assuming all static correlators and the nonergodicity parameters to be diagonal in l and l'. The reader should note that the diagonality of the nonergodicity parameters is an additional approximation. This latter approximation has been motivated by a similar investigation for a supercooled liquid of diatomic molecules [22].

The solution of the MMCT equations yields the critical temperature $T'^{MMCT}_c \cong 208$ K. In the diagonalization approximation, we also obtained a *single* transition temperature $T^{MMCT}_c \cong 206$ K, which does not differ much from T'^{MMCT}_c and $T^{MD}_c \cong 200 \pm 3K$. We consider this very good agreement as fortuitous, since usually the mode coupling theory strongly overestimates the freezing [24,25]. That the diagonalization approximation almost does not affect the transition temperature is quite different from what has been found in a similar study for diatomic molecules with Lennard-Jones interactions. There, the diagonalization approximation causes the separate freezing of the COM correlators ($l=l'=0$) and the ''orientational'' correlators with $l=l'\neq 0$ [22]. This quite different behavior is probably related to the much stronger translational–orientational coupling in the case of water.

Comparison of the MMCT results for $F_{l0,l'0}(q,m)$ with the corresponding MD results leads to the following main conclusions:

(i) $F_{l0,l'0}(q,m)$ obtained from MMCT, without and with diagonalization approximation, differ only slightly from each other, which confirms the dominance of the diagonal correlators.

(ii) The qualitative q dependence of $F_{l0,l'0}(q,m)$ from the MD simulation is well reproduced by the corresponding MMCT result. This is even true for some fine structure such as the shoulder at $q \cong 20$ nm^{-1} of $F_{10,10}(q,m=0)$.

(iii) A good *quantitative* agreement between the MD– and MMCT results is found for the full q range for $F_{10,10}(q,m=1)$ and $F_{10,00}(q,m=0)$. For the other cases, except those with $l=l'=2$, a reasonable agreement is found for $q<30$ nm^{-1}. For $F_{20,20}(q,m)$, the deviations are rather large, particularly for $q<40$ nm^{-1}.

This behavior for $F_{l0,l'0}(q,m)$ is in full accordance with that for diatomic molecules [22,25]. The larger discrepancy for the case of $l=l'=2$ is probably due to the cutoff at $l_{co}=2$. For a single dumbbell in an isotropic liquid of hard spheres, it has been shown that MMCT yields accurate results for, e.g., $F_{l0,l0}(q,m)$ if one chooses $l_{co}=l+2$ [27].

Since this first quantitative comparison of MMCT and the MD results for water is encouraging, we are planning to extend our MMCT study for water to include n and n'. This will offer the possibility of answering the interesting question of whether the 180° jumps of the protons, which leave the molecule invariant, freeze at the same critical temperature at which all the other degrees of freedom freeze, or if they will freeze at a lower temperature. Besides the nonergodicity parameters, it would also be interesting to calculate from MMCT the critical amplitudes $H_{ln,l'n'}(q,m)$ and the exponent parameter λ, from which the critical exponent a, the von Schweidler exponent b, as well as γ which characterizes the power law divergence of the α-relaxation timescale, can be obtained. Finally, a solution of the time-dependent MMCT equations would be desirable. These extensions will be hard to achieve without further approximation schemes. Our results give a strong indication that this could be possible. As the comparison of the different approximations presented in this paper demonstrates, the solutions of the MMCT are not strongly affected if small and temperature insensitive components of the *static* structure factors $S_{ln,l'n'}(q,m)$ are neglected. Therefore it should be possible to restrict the MMCT to the most relevant components, where the question of relevance is decided on the basis of the static correlation functions. Depending on the system, this procedure can lead to a dramatic reduction of memory functions to be calculated. This could enable us to capture more qualitative features of the nonergodicity parameters and dynamics, by including the relevant components with $l>2$, thereby neglecting irrelevant components with $l\leqslant 2$.

To summarize, we can say that this first quantitative test of MMCT for water has demonstrated reasonable agreement of both the critical temperature and critical nonergodicity parameters obtained from MMCT and a MD simulation, although the agreement of the transition temperatures should not be overestimated.

ACKNOWLEDGMENTS

The research of L.F., F.S., and P.T. was supported by MURST (prin 98). A.L., R.S., and C.T. gratefully acknowledge financial support by SFB 262.

APPENDIX A: SIMPLIFICATION OF THE MMCT EQUATIONS FOR WATER MOLECULES

The C_{2v} symmetry of the water molecule leads to the consequence that the molecular correlation function $S_{\kappa,\kappa'}(\vec{q},t)$ for n and n' odd are given by the self-correlations and vanish for n odd, n' even or n even, n' odd, i.e., the matrix $\mathbf{S}(\vec{q},t)$ has the block structure

$$\mathbf{S}(\vec{q},t)=\begin{array}{c|c|c} n' \text{ even} & n' \text{ odd} & \\ \hline \tilde{\mathbf{S}}(\vec{q},t) & \mathbf{0} & n \text{ even} \\ & & \\ \mathbf{0} & \tilde{\mathbf{S}}^{(s)}(\vec{q},t) & n \text{ odd} \end{array} \qquad \text{(A1)}$$

Thus the direct correlation functions $c_{\kappa,\kappa'}(\vec{q})$ are nonzero for n and n' even, only. From Eq. (12), we can conclude that the functions $v^{\alpha\mu}_{\kappa\kappa_1\kappa_2}(\vec{q},\vec{q}_1,\vec{q}_2)$ vanish if n_1 and n_2 are odd. As a consequence, the memory functions can *not* contain terms of the kind $v*v*\tilde{S}^{(s)}*\tilde{S}^{(s)}$. Considering that the factors u [see Eqs. (12), (14)] contain the Clebsch-Gordan coefficients $\mathcal{C}(l_1l_3l;n_1n_3n)$ or $\mathcal{C}(l_1l_3l;n_1+\mu\, n_3\, n+\mu)$ or the corresponding ones with $(1\leftrightarrow 2)$, where n_3 has to be even since it occurs also as an index of the direct correlation function [see Eq. (12)] one concludes that terms of the kind

$$v*v*\tilde{S}*\tilde{S} \qquad \text{(A2)}$$

are only contained in memory functions with n and n' even. Furthermore, one finds that memory functions with n and n' odd contain only terms of the kind

$$v*v*\tilde{S}*\tilde{S}^{(s)}, \qquad \text{(A3)}$$

while memory functions with different n even, n' odd or n odd, n' even, vanish. We can summarize those findings in the schematic representation

$$\underline{\mathbf{m}}(\vec{q},t)=\begin{array}{c|c|c} n' \text{ even} & n' \text{ odd} & \\ \hline vv\tilde{S}\tilde{S} & \mathbf{0} & n \text{ even} \\ & & \\ \mathbf{0} & vv\tilde{S}\tilde{S}^{(s)} & n \text{ odd} \end{array} \qquad \text{(A4)}$$

Since this block structure is also preserved under matrix inversion, the whole set of equations is split into two parts. The first part, which consists of the block with even n and n', forms a closed set of equations, since also in the calculation of the memory kernels (A2) only matrix elements with even n and n' occur. The second block depends on the solution of the first set because of the structure of the memory functions (A3) and can be shown to be identical to the tagged particle equations for the self-part.

APPENDIX B: Q-FRAME REPRESENTATION

In contrast to the case of simple liquids, the density correlator $\mathbf{S}(\vec{q},t)$ as defined in Sec. II depends on modulus and orientation of the vector $\vec{q}$. Therefore, a direct numerical implementation of the equations given above is not suitable, but further reformulations are necessary. The dependence on the direction of the ''outer'' $\vec{q}$ vector is easily removed by choosing the z axis of the laboratory frame of reference in direction of $\vec{q}$. The choice of the q frame further offers the advantage that the matrix $\mathbf{S}(\vec{q},t)$ becomes diagonal with respect to m and m', i.e.,

$$\begin{aligned} S_{lmn,l'm'n'}(q\hat{e}_z,t) &\equiv S^{m}_{ln,l'n'}(q,t)\,\delta_{m,m'} \\ &\equiv S_{ln,l'n'}(q,m,t)\,\delta_{m,m'}. \end{aligned} \qquad \text{(B1)}$$

To get a reformulation of the equations of motion in terms of the q-frame quantities, we still have to care about the ''inner'' $\vec{q}$ vectors $\vec{q}_1$ and $\vec{q}_2$ appearing in the summation of the MCT memory functions [cf. Eq. (11)]. This can be done by using the transformation law of the tensors $\mathbf{S}(\vec{q},t)$ under rotations, which gives a relation between $S_{ln,l'n'}(q,m,t)$ and the molecular correlation function for general direction of $\vec{q}$:

$$S_{lmn,l'm'n'}(\vec{q},t) = \sum_{m''} D^{l}_{mm''}(\Omega_q) D^{l'*}_{m'm''}(\Omega_q) S_{ln,l'n'}(q,m'',t), \tag{B2}$$

where Ω_q denotes the polar angles of the vector $\vec{q}$ with respect to the laboratory frame.

Thus we get the following set of MMCT equations in the *q-frame representation*:

$$\mathbf{S}(q,m,z) = -[z\mathbf{S}^{-1}(q,m) + \mathbf{S}^{-1}(q,m)\mathbf{K}(q,m,z)\mathbf{S}^{-1}(q,m)]^{-1}, \tag{B3}$$

$$K_{ln,l'n'}(q,m,z) = \sum_{\alpha\alpha'} \sum_{\mu\mu'} q^{\alpha\mu}_{ln}(q\hat{e}_z) q^{\alpha'\mu'*}_{l'n'}(q\hat{e}_z) k^{\alpha\mu,\alpha'\mu'}_{lmn,l'mn'}(q,z), \tag{B4}$$

$$\underline{\mathbf{k}} = -[z\underline{\mathbf{J}}^{-1} + \underline{\mathbf{m}}(q,z)]^{-1}, \tag{B5}$$

with **J** as given in Sec. II A. The memory functions are still nondiagonal with respect to m and m'. But one can show that they are different from zero only in the following cases:

$\alpha=T$	$\alpha'=T$	$m+\mu=m'+\mu'$
$\alpha=T$	$\alpha'=R$	$m+\mu=m'$
$\alpha=R$	$\alpha'=T$	$m=m'+\mu'$
$\alpha=R$	$\alpha'=R$	$m=m'$

(B6)

Besides the q–frame representation, we have maintained that the restricted summation over $\vec{q}_1$ and $\vec{q}_2$, which becomes an integration in the thermodynamic limit $V,N\to\infty$ with $\rho_0=\text{const}$, can be reduced to a double integral. The general expression for the memory functions in the q frame is given by

$$m^{\alpha\mu,\alpha'\mu'}_{lmn,l'm'n'}(q,t) = \frac{\rho_0}{(8\pi^2)^3}\int_0^\infty dq_1 \int_{|q-q_1|}^{q+q_1} dq_2 \frac{q_1 q_2}{q} \sum_{m_1 m_2} \sum_{l_1 l_1' l_2 l_2'} \sum_{n_1 n_1' n_2 n_2'} v^{\alpha\mu}_{ln,l_1n_1,l_2n_2}(qq_1q_2;mm_1m_2) \times v^{\alpha'\mu'*}_{l'n',l_1'n_1',l_2'n_2'}(qq_1q_2;m'm_1m_2) S_{l_1n_1,l_1'n_1'}(q_1,m_1,t)\, S_{l_2n_2,l_2'n_2'}(q_2,m_2,t), \tag{B7}$$

with the vertex functions

$$v^{\alpha\mu}_{ln,l_1n_1,l_2n_2}(qq_1q_2;mm_1m_2) = \sum_{l_3n_3} [u^{\alpha\mu}_{ln,l_3n_3,l_2n_2}(qq_1q_2;mm_1m_2)\, c_{l_3n_3,l_1n_1}(q_1,m_1) + (-1)^m u^{\alpha\mu}_{ln,l_3n_3,l_1n_1}(qq_2q_1;mm_2m_1)\, c_{l_3n_3,l_2n_2}(q_2,m_2)]. \tag{B8}$$

The coefficients u are given by

$$u^{\alpha\mu}_{ln,l_1n_1,l_2n_2}(qq_1q_2;mm_1m_2) = i^{l_1+l_2-l}(-1)^{m_2}\left[\frac{(2l_1+1)(2l_2+1)}{2l+1}\right]^{1/2} q^{\alpha\mu*}_{l_1n_1}(q_1) \times \sum_{m''} d^{l_1}_{m''m_1}(\theta_1) d^{l_2}_{m-m''m_2}(-\theta_2)\mathcal{C}(l_1l_2l;m''\,m-m''\,m)\begin{cases} \mathcal{C}(l_1l_2l;n_1n_2n) & \alpha=T \\ \mathcal{C}(l_1l_2l;n_1+\mu\,n_2\,n+\mu) & \alpha=R \end{cases}. \tag{B9}$$

The quantities d^l_{mn} are the reduced Wigner matrices [19] and the angles θ_i are determined by

$$\cos(\theta_1) = \frac{q^2+q_1^2-q_2^2}{2qq_1}\ , \quad \sin(\theta_1) = \sqrt{1-\cos(\theta_1)^2}, \tag{B10}$$

and the corresponding relations with $(1\leftrightarrow 2)$. Furthermore, we have

$$q_{ln}^{\alpha\mu}(q_i)=\begin{cases} \frac{1}{\sqrt{2}}q_i\sin(\theta_i) & \alpha=T,\mu=\pm 1\\ q_i\cos(\theta_i) & \alpha=T,\mu=0\\ \frac{1}{\sqrt{2}}\sqrt{l(l+1)-n(n+\mu)} & \alpha=R,\mu\pm 1\\ n & \alpha=R,\mu=0. \end{cases} \tag{B11}$$

It should be immediately obvious that a numerical solution of the equations of motion given here poses a formidable task. Due to the large number of summations and the occurrence of special functions, the evaluation of the memory functions will be the main computational problem.

The first step in an analysis of the equations for $\mathbf{S}(q,m,t)$ is the localization of the critical temperature T_c at which a bifurcation of the long-term behavior of the solutions takes place. Therefore, one studies the nonergodicity parameters

$$\mathbf{F}(q,m)=\lim_{t\to\infty}\mathbf{S}(q,m,t)=-\lim_{z\to 0}z\mathbf{S}(q,m,z), \tag{B12}$$

which obey the following equations:

$$\mathbf{F}(q,m)=[\mathbf{S}^{-1}(q,m)+\mathbf{S}^{-1}(q,m)\mathbf{K}(q,m)\mathbf{S}^{-1}(q,m)]^{-1}, \tag{B13}$$

$$K_{ln,l'n'}(q,m)=\sum_{\alpha\alpha'}\sum_{\mu\mu'} q_{ln}^{\alpha\mu}(q)q_{l'n'}^{\alpha'\mu'*}(q)(\underline{m}^{-1}(q))_{lmn,l'mn'}^{\alpha\mu,\alpha'\mu'}, \tag{B14}$$

$$\begin{aligned} m_{lmn,l'm'n'}^{\alpha\mu,\alpha'\mu'}(q)={}&\frac{\rho_0}{(8\pi^2)^3}\int_0^\infty dq_1\int_{|q-q_1|}^{q+q_1}dq_2\sum_{m_1m_2}\sum_{l_1l_1'l_2l_2'}\sum_{n_1n_1'n_2n_2'} v_{ln,l_1n_1,l_2n_2}^{\alpha\mu}(qq_1q_2;mm_1m_2)\\ &\times v_{l'n',l_1'n_1',l_2'n_2'}^{\alpha'\mu'*}(qq_1q_2;m'm_1m_2)F_{l_1n_1,l_1'n_1'}(q_1,m_1,t)\,F_{l_2n_2,l_2'n_2'}(q_2,m_2,t), \end{aligned} \tag{B15}$$

that have to be solved self-consistently.

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