

# Mode coupling approach to the ideal glass transition of molecular liquids: Linear molecules

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The mode coupling theory (MCT) for the ideal liquid glass transition, which was worked out for *simple* liquids mainly by Götze, Sjögren, and their co-workers, is extended to a *molecular* liquid of *linear* and *rigid* molecules. By use of the projection formalism of Zwanzig and Mori an equation of motion is derived for the correlators  $S_{lm,l'm'}(\mathbf{q},t)$  of the tensorial one-particle density  $\rho_{lm}(\mathbf{q},t)$ , which contains the orientational degrees of freedom for  $l>0$ . Application of the mode coupling approximation to the memory kernel results into a *closed* set of equations for  $S_{lm,l'm'}(\mathbf{q},t)$ , which requires the static correlators  $S_{lm,l'm'}(\mathbf{q})$  as the only input quantities. The corresponding MCT equations for the nonergodicity parameters  $f_l^m(q) \equiv f_{lm,lm}(q\mathbf{e}_3)$  are solved for a system of dipolar hard spheres by restricting the values for  $l$  to 0 and 1. Depending on the packing fraction  $\varphi$  and on the temperature  $T$ , three different phases exist: a liquid phase, where translational (TDOF's) ( $l=0$ ) and orientational (ODOF's) ( $l=1$ ) degrees of freedom are ergodic, a phase where the TDOF are frozen into a (nonergodic) glassy state, whereas the ODOF's remain ergodic, and finally a glassy phase where both, TDOF's and ODOF's, are nonergodic. From the nonergodicity parameters  $f_0^0(q)$  and  $f_1^1(q)$  for  $q=0$ , we may conclude that the corresponding relaxation strength of the  $\alpha$  peak of the compressibility can be much smaller than the corresponding strength of the dielectric function. [S1063-651X(97)02409-4]

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## I. INTRODUCTION

The use of mode coupling theory (MCT) more than a decade ago represents one of the most important steps in the theoretical description of the glassy dynamics of supercooled liquids: This theory was mainly worked out by Götze, Sjögren, and their co-workers. For reviews the reader may consult Refs. [1–3]. A complementary approach, which is based on fluctuating nonlinear hydrodynamics, was introduced later by Das and Mazenko and co-workers [4,5]. Both approaches derive a closed set of equations for the time-dependent density correlator for a *simple liquid*,

$$S_q(t) = \frac{1}{N} \langle \delta\rho^*(\mathbf{q},t) \delta\rho(\mathbf{q}) \rangle, \quad (1)$$

where  $\delta\rho(\mathbf{q},t) = \rho(\mathbf{q},t) - \langle \rho(\mathbf{q},t) \rangle$  is the fluctuation of the Fourier-transformed one-particle density  $\rho(\mathbf{x},t)$ . Taking the normalized correlator  $\phi_q(t) = S_q(t)/S_q$ , with  $S_q = S_q(t=0)$  the static correlator, the MCT equations are as follows:

$$\ddot{\phi}_q(t) + \Omega_q^2 \phi_q(t) + \int_0^t dt' M_q(t-t') \dot{\phi}_q(t') = 0, \quad (2a)$$

where  $\Omega_q$  is the microscopic frequency:

$$\Omega_q^2 = \frac{kT}{m} q^2 / S_q. \quad (2b)$$

Separating the fast and slow parts, the memory kernel  $M_q(t)$  can be decomposed as follows:

$$M_q(t) = 2\nu_q \delta(t) + \Omega_q^2 m_q(t), \quad (2c)$$

with the bare friction  $\nu_q$  and

$$m_q(t) = \frac{1}{2N} \sum_{\mathbf{q}_1, \mathbf{q}_2} V(\mathbf{q}; \mathbf{q}_1, \mathbf{q}_2) \phi_{q_1}(t) \phi_{q_2}(t). \quad (2d)$$

The summation in Eq. (2d) is restricted to  $\mathbf{q}_1, \mathbf{q}_2$  such that  $\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q}$  due to translational symmetry. The vertices  $V(\mathbf{q}; \mathbf{q}_1, \mathbf{q}_2)$  which characterize the coupling between a pair of density modes, depend on the static density correlator only. Therefore (apart from  $\nu_q$ ), the dynamics is uniquely determined by the static correlator  $S_q$ . We also mention that the right hand side of Eq. (2d) is the first term in a polynomial expansion of  $m_q(t)$  into products

$$\phi_{q_1}(t) \cdots \phi_{q_m}(t) \quad \text{with } m \geq 2.$$

Let us give a brief summary of the results which follow from Eqs. (1) and (2) (for details, see Refs. [1–3]). The first important result is the existence of a critical temperature  $T_c$  (or a critical density  $\rho_c$ ) at which a *dynamical transition* takes place from an ergodic to a nonergodic phase. This transition can be interpreted as a glass transition. As an order parameter one chooses the *nonergodicity parameter*

$$f_q = \lim_{t \rightarrow \infty} \phi_q(t), \quad (3)$$

which vanishes in the ergodic phase, for  $T > T_c$ , and is positive for  $T \leq T_c$ .  $f_q$  may change continuously (type-A transition) or discontinuously (type-B transition). Let us restrict ourselves to the type-B transition, which is relevant for structural glass transitions. Then, in the vicinity of  $T_c$ , two scaling law regimes occur with time scales  $t_\sigma$  and  $\tau$ . For the  $\alpha$ -relaxation regime, where  $t$  is of order  $\tau$ , there exists a master function  $\bar{\phi}_q(\bar{t})$  such that

$$\phi_q(t, T) = \bar{\phi}_q(t/\tau(T)). \quad (4)$$

In the so-called  $\beta$ -relaxation regime (not to be confused with the  $\beta$  process), one finds the power-law behavior

$$\phi_q(t, T) - f_q^c \sim \begin{cases} (t/t_\sigma(T))^{-a}, & t_0 \ll t \ll t_\sigma \\ -(t/\tau(T))^b, & t_\sigma \ll t \ll \tau. \end{cases} \quad (5a)$$

$$(5b)$$

$f_q^c \equiv f_q(T_c)$  is the nonergodicity parameter at  $T_c$ , and  $t_0 \approx \Omega_q^{-1}$  is a microscopic time scale. The temperature dependence of  $t_\sigma$  and  $\tau$  is given by

$$t_\sigma(T) \sim |T - T_c|^{-1/2a} \quad (6a)$$

and

$$\tau(T) \sim (T - T_c)^{-\gamma}, \quad T \geq T_c \quad (6b)$$

with  $\gamma = (1/2a) + (1/2b)$ . The two positive exponents  $a$  and  $b$  which are the scaling exponents of the *critical law* (5a) and the *von Schweidler law* (5b), respectively, follow from the exponent parameter  $\lambda$  ( $0 < \lambda < 1$ ):

$$\frac{(\Gamma(1-a))^2}{\Gamma(1-2a)} = \lambda = \frac{(\Gamma(1+b))^2}{\Gamma(1+2b)}, \quad (7)$$

where  $\Gamma$  is the gamma function.  $\lambda$  depends on the vertices at  $T_c$ . The scaling laws (4) and (5) only involve quantities which can be deduced if the explicit  $T$  dependence of the vertices is known. It is this fact which demonstrates the strength of MCT as a microscopic theory of the glass transition. The version described above is called the *idealized MCT*.

Das and Mazenko [5] discovered that the glass transition singularity at  $T_c$  is smeared out due to contributions to  $m_q(t)$  originating from a coupling to the current density. The same conclusion was found later by Götze and Sjögren [6]. The latter authors identified hopping processes to be responsible for restoring ergodicity. Another interesting MCT approach was recently given in Ref. [7]. Assuming that detailed balance holds, it was proven that no sharp transition temperature exists. There was a controversy between the results of Refs. [5, 7] and of Ref. [6] concerned with the behavior of the  $\alpha$ -peak width for  $q \rightarrow 0$ , which, however, was recently clarified by Latz and Schmitz [8]. Despite the necessity to use this *extended MCT*, several experimental (e.g., Refs. [2, 3]) and numerical investigations (e.g., Refs. [9–12]) have clearly demonstrated the existence of a signature of the glass transition singularity and the validity of the power laws (5a) and (5b) for a couple of glass forming systems.

However, it is not quite obvious whether the dielectric relaxation results are consistent with the predictions of the idealized MCT. Since the orientational degrees of freedom (ODOF's), which are probed by dielectric spectroscopy, couples to the translational degrees of freedom (TDFOS's), i.e., to the density fluctuations, MCT predicts for, e.g., the dipole correlator, a power-law behavior as described by Eq. (5) with the *same* exponents. This implies that the imaginary part  $\kappa_q''(\omega)$  and  $\varepsilon''(\omega)$  of the compressibility and dielectric function, respectively, exhibit for  $T > T_c$  a minimum at the *same* frequency  $\omega_{\min}$ . Whereas  $\kappa_q''(\omega)$ , obtained from light and neutron scattering experiments, shows a MCT minimum

for glycerol [13], salol [14], CKN [15,6], and OTP [17], no minimum was found in the dielectric experiments for glycerol [18] and salol [18]. For OTP,  $\varepsilon''(\omega)$  possesses a  $\beta$  peak [19] such that a minimum exists. But its position is at much smaller frequencies than the corresponding minimum in  $\kappa_q''(\omega)$ . Increasing the high-frequency range by more than an order of magnitude, Loidl and co-workers very recently found a minimum in  $\varepsilon''(\omega)$  for glycerol [20] and CKN [21]. Whereas its position is in reasonable agreement for CKN with the light [16] and neutron scattering data [15], this is not the case for glycerol. For Salol [22], only *evidence* of the existence of a minimum in  $\varepsilon''(\omega)$  has been found, without specifying its position. The status of OTP is still unclear.

This situation, and the fact that most glass formers in nature are *molecular liquids*, suggest an extension of MCT to molecular liquids in order to investigate also the dynamics of the ODOF and the role of coupling between TDOF's and ODOF's. Apart from the orientational glass phases of mixed crystals [23] for which MCT was worked out by Bostoen and Michel [24], no such MCT approach exists for molecular liquids. It is the main purpose of our contribution to extend MCT to a molecular liquid of *linear* molecules. A similar investigation was performed for a single linear molecule in a simple liquid by Franosch *et al.* [25], and for a molecular liquid using fluctuating nonlinear hydrodynamics by Schmitz [26]. A short account of part of our work was already given in Ref. [27].

Of course, there exists a huge literature concerning the orientational dynamics. For instance, one approach is the use of a Smoluchowski equation. However, this equation is usually linearized, which may lead to exponential relaxation. For more detail the reader is referred to the recent review by Bagchi and Chandra [28]. There is strong numerical evidence from molecular dynamics simulations that even ODOF's do exhibit nonexponential relaxation in the supercooled molecular liquid [9,29–32]. Another review, by Madden and Kivelson [33], is recommended as well. There, e.g., a “three-variable” theory is discussed. Using the Mori-Zwanzig formalism, a three-step continued fraction for a correlator is derived where a Markov approximation is performed for the resulting memory kernel. This approach may be reasonable in the weakly supercooled liquid, but its validity in the strongly supercooled regime is not obvious. Furthermore a continued fraction of an *odd* number of steps can never lead to a glass transition singularity as described by MCT [1–3].

Therefore, we believe that our extension of MCT to supercooled molecular liquids may complement earlier work. Our paper is organized as follows. Section II presents the various correlation functions and its symmetry properties. The MCT approach is discussed in its general form for linear molecules in Sec. III and applied to a system of dipolar hard spheres in Sec. IV. Section V contains a discussion of our results and some conclusions. To avoid too much technical calculations in the text, several appendices have been added where the interested reader may learn more details of the specific calculation.

## II. CORRELATION FUNCTIONS

In this section we present the correlations functions which we will investigate, as well as their symmetry properties. We

consider a system of  $N$ -linear and rigid molecules with mass  $M$  and inertia tensor  $\mathbf{I}$  contained in a volume  $V$ . TDOF's are specified by  $\{\mathbf{x}_n\} = (\mathbf{x}_1, \dots, \mathbf{x}_N)$  and  $\{\mathbf{p}_n\} = \{\mathbf{p}_1, \dots, \mathbf{p}_N\}$ , where  $\mathbf{x}_n$  and  $\mathbf{p}_n = m\mathbf{v}_n$  are the center-of-mass position and momentum of the  $n$ th molecule, respectively. For the ODOF one may also use a canonical description [25], but here we choose  $\{\Omega_n\} = (\Omega_1, \dots, \Omega_N)$  and  $\{\mathbf{l}_n\} = (\mathbf{l}_1, \dots, \mathbf{l}_N)$  as orientational coordinates, where  $\Omega_n = (\phi_n, \theta_n)$  are the Euler angles of the  $n$ th molecule, and  $\mathbf{l}_n = \mathbf{I}(\Omega_n)\boldsymbol{\omega}_n$  is the corresponding angular momentum. The linear and angular velocities are, respectively,  $\mathbf{v}_n$  and  $\boldsymbol{\omega}_n$ . The third Euler angle  $\chi_n$  will be redundant, due to the cylindrical symmetry of our molecules. With  $V(\{\mathbf{x}_n\}, \{\Omega_n\})$  the potential energy, the classical energy of our molecular system is given by

$$H(\{\mathbf{x}_n\}, \{\mathbf{p}_n\}, \{\Omega_n\}, \{\mathbf{l}_n\}) = \sum_{n=1}^N \left[ \frac{1}{2M} \mathbf{p}_n^2 + \frac{1}{2} \mathbf{l}_n^T \mathbf{I}^{-1}(\Omega_n) \mathbf{l}_n \right] + V(\{\mathbf{x}_n\}, \{\Omega_n\}), \quad (8)$$

where  $\mathbf{l}_n^T$  is the transposed of  $\mathbf{l}_n$  and the  $\Omega_n$  dependence of  $\mathbf{I}$  in the laboratory frame  $K$  has been made explicit. The corresponding quantities in the body fixed frame  $K'$  are obtained from those in  $K$  by a rotation  $\mathbf{R}(\phi_n, \theta_n)$ . For instance, it is

$$\mathbf{l}'_n = \mathbf{I} d\mathbf{R}(\Omega_n) \mathbf{l}_n, \quad \boldsymbol{\omega}'_n = \mathbf{R}(\Omega_n) \boldsymbol{\omega}_n \quad (9)$$

and

$$\mathbf{I}' = \mathbf{R}(\Omega_n) \mathbf{I}(\Omega_n) \mathbf{R}^{-1}(\Omega_n) = \begin{pmatrix} I & 0 & 0 \\ 0 & I & 0 \\ 0 & 0 & I' \end{pmatrix}, \quad (10)$$

where the body fixed frame of the  $n$ th molecule can be chosen such that  $\mathbf{I}'$  is diagonal.

The most basic quantity for the description of a liquid is the time-dependent, *microscopic* one-particle density

$$\rho(\mathbf{x}, \Omega, t) = \sum_{n=1}^N \delta(\mathbf{x}_n - \mathbf{x}_n(t)) \delta(\Omega_n, \Omega_n(t)). \quad (11)$$

$\delta(\Omega, \Omega')$  denotes the invariant delta function. For this and many other details of the theoretical description of fluids with ODOF which will be used throughout this paper, the reader is referred to the excellent textbook by Gray and Gubbins [34]. Any function  $f(\mathbf{x}, \Omega)$  can be expanded with respect to plane waves and spherical harmonics:

$$f(\mathbf{x}, \Omega) = \frac{1}{V} \frac{1}{\sqrt{4\pi}} \sum_q \sum_{l,m} (-i)^l f_{lm}(\mathbf{q}) e^{-i\mathbf{q} \cdot \mathbf{x}} Y_{lm}^*(\Omega), \quad (12)$$

with the coefficients

$$f_{lm}(\mathbf{q}) = \sqrt{4\pi} i^l \int_V d^3x \int d^2\Omega f(\mathbf{x}, \Omega) e^{i\mathbf{q} \cdot \mathbf{x}} Y_{lm}(\Omega). \quad (13)$$

The factor  $(\pm i)^l$  is used for technical convenience, as will be seen below. Substitution of Eq. (11) into Eq. (13) yields the tensorial density modes:

$$\rho_{lm}(\mathbf{q}, t) = \sqrt{4\pi} i^l \sum_{n=1}^N e^{i\mathbf{q} \cdot \mathbf{x}_n(t)} Y_{lm}(\Omega_n(t)). \quad (14)$$

Then the generalization of the density correlator (1) is straightforward:

$$S_{lm;l'm'}(\mathbf{q}, t) = \frac{1}{N} \langle \delta\rho_{lm}^*(\mathbf{q}, t) \delta\rho_{l'm'}(\mathbf{q}) \rangle, \quad (15)$$

with

$$\delta\rho_{lm}(\mathbf{q}, t) = \rho_{lm}(\mathbf{q}, t) - \langle \rho_{lm}(\mathbf{q}, t) \rangle.$$

This correlator vanishes for  $\mathbf{q} = 0$ ,  $(l, m) = (l', m') = (0, 0)$ , and otherwise it is given by

$$S_{lm;l'm'}(\mathbf{q}, t) = \frac{4\pi}{N} i^{l'-l} \sum_{n,n'} \langle e^{-i\mathbf{q} \cdot (\mathbf{x}_n(t) - \mathbf{x}_{n'})} \times Y_{lm}^*(\Omega_n(t)) Y_{l'm'}(\Omega_{n'}) \rangle. \quad (16)$$

For later purposes we also introduce the *translational* ( $\alpha = T$ ) and *rotational* ( $\alpha = R$ ) current density

$$\mathbf{j}_{lm}^\alpha(\mathbf{q}, t) = \sqrt{4\pi} i^l \sum_{n=1}^N \mathbf{v}_n^\alpha(t) e^{i\mathbf{q} \cdot \mathbf{x}_n(t)} Y_{lm}(\Omega_n(t)), \quad (17)$$

with

$$\mathbf{v}_n^\alpha(t) = \begin{cases} \mathbf{v}_n(t), & \alpha = T \\ \boldsymbol{\omega}_n(t), & \alpha = R, \end{cases} \quad (18)$$

and the corresponding current density correlator

$$\begin{aligned} J_{lm;l'm'}^{\alpha k; \alpha' k'}(\mathbf{q}, t) &= \frac{1}{N} \langle j_{lm}^{\alpha k*}(\mathbf{q}, t) j_{l'm'}^{\alpha' k'}(\mathbf{q}) \rangle \\ &= \frac{4\pi}{N} i^{l'-l} \sum_{n,n'} \langle v_n^{\alpha k}(t) v_{n'}^{\alpha' k} \\ &\quad \times e^{-i\mathbf{q} \cdot (\mathbf{x}_n(t) - \mathbf{x}_{n'})} Y_{lm}^*(\Omega_n(t)) Y_{l'm'}(\Omega_{n'}) \rangle \end{aligned} \quad (19)$$

where, e.g.,  $j_{lm}^{\alpha k}$ ,  $k = 1, 2$ , and 3 are the Cartesian coordinates of  $\mathbf{j}_{lm}^\alpha$ .  $\rho_{lm}$  and  $\mathbf{j}_{lm}^\alpha$  are related by the *continuity equation*

$$i\mathcal{L}\rho_{lm}(\mathbf{q}, t) \equiv \dot{\rho}_{lm}(\mathbf{q}, t) = i \sum_\alpha (\hat{\mathbf{q}}^\alpha \mathbf{j}^\alpha)_{lm}(\mathbf{q}, t), \quad (20)$$

where  $\mathcal{L}$  is the corresponding Liouvillean, and as a shorthand notation we use the operator

$$\hat{\mathbf{q}}^\alpha = \begin{cases} \mathbf{q}, & \alpha = T \\ \mathbf{L}, & \alpha = R, \end{cases} \quad (21)$$

with  $\mathbf{L}$  the angular momentum operator. Its action on a function  $f_{lm}(q)$  is defined as follows:

$$(\hat{q}^{\alpha k} f)_{lm}(\mathbf{q}) = \begin{cases} q^k f_{lm}(\mathbf{q}), & \alpha = T \\ \sum_{m'=-l}^l L_{l,mm'}^k f_{lm'}(\mathbf{q}), & \alpha = R, \end{cases} \quad (22)$$

where

$$L_{l,mm'}^1 \pm iL_{l,mm'}^2 \equiv L_{l,mm'}^\pm = [l(l+1) - m(m \pm 1)]^{1/2} \delta_{m', m \pm 1}, \quad (23)$$

$$L_{l,mm'}^3 = m \delta_{m'm}.$$

Now we discuss the various properties of  $S_{lm;l'm'}(\mathbf{q}, t)$ . Similar properties hold for  $J_{lm;l'm'}^{\alpha k; \alpha' k'}(\mathbf{q}, t)$ . This discussion is like that of Blum and Torruella [35], who used an expansion into rotational invariants.

Since the time-dependent quantities  $\mathbf{x}_n(t)$ ,  $\Omega_n(t)$ , etc. follow from the (microscopic) Newtonian dynamics for given initial conditions  $\{\mathbf{x}_n\}$ ,  $\{\Omega_n\}$ , etc., time translation and time reversal symmetry holds. Taking this into account, it immediately follows from definition (15) that

$$S_{lm;l'm'}^*(\mathbf{q}, t) = S_{l'm';lm}(\mathbf{q}, t), \quad (24)$$

i.e., the matrix  $S(\mathbf{q}, t) = (S_{lm;l'm'}(\mathbf{q}, t))$  is *Hermitian*. On the other hand, we may use Eq. (16) and the behavior of  $Y_{lm}(\Omega)$  under complex conjugation. This yields

$$S_{lm;l'm'}^*(\mathbf{q}, t) = (-1)^{l+l'+m+m'} S_{l-m;l'-m'}(-\mathbf{q}, t), \quad (25)$$

$\rho_{lm}(\mathbf{q}, t; X)$  is a tensor field of rank  $l$ . Here we also explicitly included the dependence on the initial conditions which are symbolically denoted by  $X$ . Then, the following transformation law for rotations  $R \in \text{SO}(3)$  holds:

$$\rho_{lm}(R\mathbf{q}, t; RX) = \sum_{m'=-l}^l D_{m'm}^l(R) \rho_{lm'}(\mathbf{q}, t; X), \quad (26)$$

where  $RX$  is used for the rotated initial conditions and  $D_{m'm}^l(R)$  are Wigner's generalized spherical harmonics [34]. Similarly one has

$$j_{lm}^{\alpha k}(R\mathbf{q}, t; RX) = \sum_{k'=1}^3 \sum_{m'=-l}^l R_{kk'} D_{m'm}^l(R) j_{lm'}^{\alpha k'}(\mathbf{q}, t; X). \quad (27)$$

The angular brackets in Eqs. (15), (16), and (19) denote the canonical average over the initial conditions  $X$ . By assumption it is  $H(RX) \equiv H(X)$ . Therefore, Eqs. (26) and (27) imply the transformation law for the correlators

$$S_{lm;l'm'}(R\mathbf{q}, t) = \sum_{m_1, m_1'} D_{m_1 m}^{l*}(R) D_{m_1' m'}^{l'}(R) S_{lm_1;l'm_1'}(\mathbf{q}, t) \quad (28)$$

and

$$J_{lm;l'm'}^{\alpha k; \alpha' k'}(R\mathbf{q}, t) = \sum_{k_1, k_1'} \sum_{m_1, m_1'} R_{kk_1} R_{k'k_1'} D_{m_1 m}^{l*}(R) D_{m_1' m'}^{l'}(R) \times J_{lm_1;l'm_1'}^{\alpha k_1; \alpha' k_1'}(\mathbf{q}, t). \quad (29)$$

What remains is the behavior under *inversion*  $P$ . Since  $Y_{lm}(P\Omega) = (-1)^l Y_{lm}(\Omega)$ , it follows from Eqs. (16) and (19) that

$$S_{lm;l'm'}(-\mathbf{q}, t) = (-1)^{l+l'} S_{lm;l'm'}(\mathbf{q}, t) \quad (30)$$

and

$$J_{lm;l'm'}^{\alpha k; \alpha' k'}(-\mathbf{q}, t) = (-1)^{l+l'} \varepsilon_\alpha \varepsilon_{\alpha'} J_{lm;l'm'}^{\alpha k; \alpha' k'}(\mathbf{q}, t), \quad (31)$$

respectively, where  $\varepsilon_T = -1$  and  $\varepsilon_R = 1$ .

It is more convenient to represent these correlators in the  $q$  frame [34], i.e., in the laboratory frame where  $\mathbf{q} = \mathbf{q}_0 \equiv (0, 0, q)$  and  $q = |\mathbf{q}|$ . For rotations  $R_3(\phi) \equiv R(\phi, \theta=0, \chi=0)$  around the  $z$  axis, it is  $D_{m'm}^l(R) = e^{-im\phi} \delta_{mm'}$  [34]. In that case we obtain, from Eq. (28),

$$S_{lm;l'm'}(\mathbf{q}_0, t) = e^{i(m-m')\phi} S_{lm;l'm'}(\mathbf{q}_0, t),$$

which must hold for all  $\phi$ . Therefore,  $S_{lm;l'm'}(\mathbf{q}_0, t)$  must be *diagonal* in  $m$  and  $m'$ :

$$S_{lm;l'm'}(\mathbf{q}_0, t) \equiv S_{ll'}^m(q, t) \delta_{mm'}. \quad (32)$$

For the current density correlator this is true for  $J_{lm;l'm'}^{\alpha 3; \alpha' 3}(\mathbf{q}_0, t)$  only.

Let us now consider the rotation  $R_2 \equiv R(0, \theta=\pi, 0)$ , which transforms  $\mathbf{q}_0$  into  $-\mathbf{q}_0$ . With  $D_{m'm}^l(R_2) = (-1)^{l+m} \delta_{m,-m'}$  [34], from (28) we obtain

$$S_{lm;l'm'}(-\mathbf{q}_0, t) = (-1)^{l+l'+m+m'} S_{l-m;l'-m'}(\mathbf{q}_0, t), \quad (33)$$

which together with Eqs. (25) and (32) yields

$$(S_{ll'}^m(q, t))^* = S_{ll'}^m(q, t), \quad (34)$$

i.e., the correlator  $S_{ll'}^m(q, t)$  is real.

Finally, it follows from Eqs. (25), (34), and (33) for  $\mathbf{q} = \mathbf{q}_0$ ,

$$S_{ll'}^m(q, t) = S_{ll'}^{-m}(q, t). \quad (35)$$

Hence for given  $q, l$  and  $l'$  the independent density correlators belong to the helicity  $m=0, 1, \dots, \min(l, l')$ .

### III. MODE-COUPLING APPROACH

The correlators  $S_{lm;l'm'}(\mathbf{q}, t)$  are of experimental and theoretical interest. For  $l=l'=0$  it describes the dynamics of the TDOF which can be measured by neutron scattering. If the molecules possess a permanent dipolar moment, the correlator with  $l=l'=1$  contains information which can be obtained from dielectric measurements and  $l=l'=2$  is related to the orientational contribution to light scattering.

In the following we will apply the Mori-Zwanzig projection formalism [36,37] in order to derive an equation of motion for  $S_{lm,l'm'}(q,t)$ . The following shorthand notation is convenient:  $(\mathbf{q},l,m)=0$ ,  $(\mathbf{q},l',m')=0'$ ,  $(\mathbf{q}_i,l_i,m_i)=i$ , and  $(l,m)=\lambda$ . The use of this formalism requires the specification of the slow variables. Because we study glassy dynamics, it is obvious that  $\delta\rho_{lm}(q)\equiv\delta\rho(0)$  is a slow variable. Then it is natural to choose  $\delta\dot{\rho}(0)$  as well. Whereas this works for *simple* liquids, leading to the MCT equations (2), it does not for *molecular* liquids. The reason is as follows: one does not expect the long-time relaxation (e.g., the structural relaxation) to show inertia effects. Consequently, the MCT equations which yield the long-time dynamics should not involve  $M$  and  $I$ . As we will see below, the simplest choice (cf. Ref. [25]) fulfilling this requirement is to take, besides  $\delta\rho(0)$ , the ‘‘longitudinal’’ translational and rotational current densities

$$j^\alpha(0)\equiv j_{lm}^\alpha(\mathbf{q})=\frac{1}{q_l^\alpha(\mathbf{q})}(\hat{\mathbf{q}}^\alpha\mathbf{J}^\alpha)_{lm}(\mathbf{q}) \quad (36)$$

for  $\alpha=T$  and  $R$ , where

$$q_l^\alpha(\mathbf{q})=\begin{cases} q, & \alpha=T \\ \sqrt{l(l+1)}, & \alpha=R. \end{cases} \quad (37)$$

A more general option, to project on each Cartesian component  $j^{\alpha k}(0)$  for  $\alpha=T,R$  and  $k=1,2,3$  (see, e.g., Ref. [38]) which generates a *coupling* between the *longitudinal* and *transversal* components of the current density, is under investigation. The energy density  $\varepsilon_{lm}(\mathbf{q})$  will be omitted as a slow variable, as it was done for a simple liquid [1].

Now we introduce the following two *projectors*:

$$P_\rho=\frac{1}{N}\sum_{\lambda\lambda'}|\delta\rho(0)\rangle\mathbf{S}^{-1}(0,0')\langle\delta\rho(0')^*| \quad (38)$$

and

$$P_j=\frac{1}{N}\sum_{\lambda\lambda'}\sum_{\alpha\alpha'}|j^\alpha(0)\rangle\mathbf{J}^{-1}(0\alpha;0'\alpha')\langle j^{\alpha'}(0')^*|. \quad (39)$$

The matrix  $\mathbf{J}\equiv(J(0\alpha;0'\alpha'))$  is given by

$$\begin{aligned} J_{lm;l'm'}^{\alpha\alpha'}(\mathbf{q}) &= \frac{1}{N}\langle j_{lm}^\alpha(\mathbf{q})^*j_{l'm'}^{\alpha'}(\mathbf{q})\rangle \\ &= \frac{kT}{I_\alpha}\delta_{ll'}\delta_{mm'}\delta_{\alpha\alpha'}, \end{aligned} \quad (40)$$

where the latter equality is proven in Appendix A.  $I_\alpha$  is the unified notation

$$I_\alpha=\begin{cases} M, & \alpha=T \\ I, & \alpha=R. \end{cases} \quad (41)$$

Making use of these projectors, it is straightforward to derive the two-step continued fraction for the Laplace transform,

$$\hat{\mathbf{S}}(\mathbf{q},z)\equiv(\hat{S}(0,0';z))=i\int_0^\infty dt \mathbf{S}(\mathbf{q},t)e^{izt}, \quad \text{Im } z>0, \quad (42)$$

of the density correlator:

$$\hat{\mathbf{S}}(\mathbf{q},z)=-[z\mathbf{1}+\hat{\mathbf{K}}(\mathbf{q},z)\mathbf{S}^{-1}(\mathbf{q})]^{-1}\mathbf{S}(\mathbf{q}), \quad (43)$$

with

$$\hat{K}_{lm;l'm'}(\mathbf{q},z)=\sum_{\alpha\alpha'}q_l^\alpha(\mathbf{q})q_{l'}^{\alpha'}(\mathbf{q})\hat{k}_{lm;l'm'}^{\alpha\alpha'}(\mathbf{q},z). \quad (44)$$

For the momentum density correlator the next projection step yields

$$\hat{\mathbf{k}}(\mathbf{q},z)=-[z\mathbf{J}^{-1}+\mathbf{J}^{-1}\hat{\mathbf{M}}(\mathbf{q},z)\mathbf{J}^{-1}]^{-1}, \quad (45)$$

where the matrix elements of the *memory kernel*  $\hat{\mathbf{M}}(\mathbf{q},z)$  are given by

$$\hat{M}_{lm;l'm'}^{\alpha\alpha'}(\mathbf{q},z)=\frac{1}{N}\left\langle\mathcal{L}j_{lm}^\alpha(\mathbf{q})^*\left|Q\frac{1}{Q\mathcal{L}Q-z}Q\left|\mathcal{L}j_{l'm'}^{\alpha'}(\mathbf{q})\right.\right\rangle. \quad (46)$$

Here,  $Q=1-P=1-(P_\rho+P_j)$  projects perpendicularly to  $\delta\rho$ ,  $j^T$  and  $j^R$ . These equations are still exact. To obtain a closed set of equations we apply a *mode-coupling approximation* for the fluctuating force  $|F_{lm}^\alpha(\mathbf{q})\rangle=Q|\mathcal{L}j_{lm}^\alpha(\mathbf{q})\rangle$ . Since the interaction between the molecules is assumed to be *pairwise*, we project  $|F_{lm}^\alpha(\mathbf{q})\rangle$  onto a product of *two* density modes. This is done in a close relationship to the case of a simple liquid which was clearly discussed by Götze [1]. Following Ref. [1], we define the projector on pairs of modes:

$$P=\sum_{11'}\sum_{22'}|\delta\rho(1)\delta\rho(2)\rangle g(12|1'2')\langle\delta\rho(1')^*\delta\rho(2')^*|, \quad (47)$$

where the normalization matrix  $g$  must fulfill

$$\begin{aligned} \sum_{1''2''}g(12|1''2'')\langle\delta\rho(1'')^*\delta\rho(2'')^*|\delta\rho(1')\delta\rho(2')\rangle \\ =\delta(12|1'2'), \end{aligned} \quad (48)$$

with the symmetrized Kronecker delta

$$\delta(12|1'2')=\frac{1}{2}[\delta(1,1')\delta(2,2')+\delta(1,2')\delta(2,1')], \quad (49)$$

and the obvious meaning  $\delta(1,1')\equiv\delta_{q_1q_1},\delta_{l_1l_1},\delta_{m_1m_1}$ . Using the approximations

$$(i) \quad |F^\alpha(0)\rangle\approx\mathcal{P}|F^\alpha(0)\rangle, \quad (50)$$

$$(ii) \quad \langle\delta\rho(1)^*\delta\rho(2)^*|Qe^{-iQ\mathcal{L}Qt}Q|\delta\rho(1')\delta\rho(2')\rangle \\ \approx N^2[S(1,1';t)S(2,2';t)+(1'\leftrightarrow 2')], \quad (51)$$

$$(iii) \quad g(12|1'2')\approx\frac{1}{4N^2}[S^{-1}(1,1')S^{-1}(2,2') \\ +(1'\leftrightarrow 2')], \quad (52)$$

we obtain

$$\begin{aligned}
M^{\alpha\alpha'}(0,0';t) &\approx \frac{1}{2N^3} \sum_{12'2'} \sum_{343'4'} \mathbf{S}^{-1}(1,1') \mathbf{S}^{-1}(2,2') \\
&\times \mathbf{S}^{-1}(3,3') \mathbf{S}^{-1}(4,4') \langle \mathcal{L}j^\alpha(0) \rangle^* \\
&\times \mathcal{Q} | \delta\rho(1) \delta\rho(2) \rangle \langle \delta\rho^*(3') \delta\rho^*(4') \rangle \\
&\times | \mathcal{Q} \mathcal{L}j^\alpha(0') \rangle S(1',3;t) S(2',4;t). \quad (53)
\end{aligned}$$

In Appendixes B and C it is shown that

$$\begin{aligned}
\langle \mathcal{L}j_\lambda^\alpha(\mathbf{q}) \rangle^* \mathcal{Q} | \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle &\approx -\frac{\rho_0}{4\pi} N \delta_{\mathbf{q}_1+\mathbf{q}_2,\mathbf{q}} \frac{kT}{I_\alpha} \\
&\times \sum_{\lambda_1''\lambda_2''} [u^\alpha(\mathbf{q}\lambda|\mathbf{q}_1\lambda_1'';\mathbf{q}_2\lambda_2'') c_{\lambda_1''\lambda_2''}(\mathbf{q}_1) S_{\lambda''\lambda_1}(\mathbf{q}_1) \\
&\times S_{\lambda_2''\lambda_2}(\mathbf{q}_1) + (1 \leftrightarrow 2)], \quad (54)
\end{aligned}$$

with

$$u^\alpha(\mathbf{q}\lambda|\mathbf{q}_1\lambda_1;\mathbf{q}_2\lambda_2) = b_{l_1 l_2 l}^\alpha(\mathbf{q}\cdot\mathbf{q}_1) C(l_1 l_2 l; m_1 m_2 m) \quad (55)$$

and

$$\begin{aligned}
b_{l_1 l_2 l}^\alpha(\mathbf{q}\cdot\mathbf{q}_1) &= i^{l_1+l_2-l} \left( \frac{(2l_1+1)(2l_2+1)}{2l+1} \right)^{1/2} \frac{1}{2} [1 + (-1)^{l_1+l_2+l}] \\
&\times \begin{cases} \frac{1}{q} (\mathbf{q}\cdot\mathbf{q}_1) C(l_1 l_2 l; 000), & \alpha=T \\ \sqrt{l_1(l_1+1)} C(l_1 l_2 l; 101), & \alpha=R, \end{cases} \quad (56)
\end{aligned}$$

where  $C(l_1 l_2 l; m_1 m_2 m)$  are the Clebsch-Gordan coefficients. The direct correlation function matrix  $(c_{\lambda\lambda'}(\mathbf{q})) = \mathbf{c}(\mathbf{q})$  is related to the static correlator  $\mathbf{S}(\mathbf{q})$  by

$$\mathbf{S}(\mathbf{q}) = \left[ 1 - \frac{\rho_0}{4\pi} \mathbf{c}(\mathbf{q}) \right]^{-1}, \quad (57)$$

and  $\rho_0 = N/V$  is the average number density. The reader should note that the prefactor  $(kT/I_\alpha)(kT/I_{\alpha'})$  which appears for  $M^{\alpha\alpha'}(0,0';t)$  after substitution of Eq. (54) into Eq. (53), is just cancelled in the combination  $\mathbf{J}^{-1}\mathbf{M}(\mathbf{q},t)\mathbf{J}^{-1}$  [which enters  $\hat{\mathbf{k}}(\mathbf{q},z)$  as Laplace transform] due to Eq. (40). Therefore, inertia effects enter only via the first term  $z\mathbf{J}^{-1}$  of  $\hat{\mathbf{k}}$ . This term, however, can be neglected in the asymptotic time regime  $t \rightarrow \infty$  which corresponds to  $z \rightarrow 0$  [1–3]. It can easily be verified that this cancellation does not occur if  $\delta\rho(0)$  and  $\delta\dot{\rho}(0)$  are used as slow variables. Putting all this together we arrive at the mode coupling expression for the slow part  $\mathbf{m}(\mathbf{q},t)$  of  $\mathbf{J}^{-1}\mathbf{M}(\mathbf{q},t)\mathbf{J}^{-1}$ ,

$$\begin{aligned}
&[(\mathbf{J}^{-1}\mathbf{M}(\mathbf{q},t)\mathbf{J}^{-1})_{\lambda\lambda'}^{\alpha\alpha'}]_{\text{slow}} \\
&\approx m_{\lambda\lambda'}^{\alpha\alpha'}(\mathbf{q},t) \\
&= \frac{1}{2N} \sum_{\mathbf{q}_1\mathbf{q}_2} \sum_{\substack{\lambda_1\lambda_1' \\ \lambda_2\lambda_2'}} V^{\alpha\alpha'}(\mathbf{q}\lambda\lambda'|\mathbf{q}_1\lambda_1\lambda_1';\mathbf{q}_2\lambda_2\lambda_2') \\
&\times S_{\lambda_1\lambda_1'}(\mathbf{q}_1,t) S_{\lambda_1\lambda_1'}(\mathbf{q}_2,t), \quad (58)
\end{aligned}$$

with the vertices

$$\begin{aligned}
V^{\alpha\alpha'}(\mathbf{q}\lambda\lambda'|\mathbf{q}_1\lambda_1\lambda_1';\mathbf{q}_2\lambda_2\lambda_2') &= \left( \frac{\rho_0}{4\pi} \right)^2 \left( \sum_{\lambda''} v^\alpha(\mathbf{q}\lambda|\mathbf{q}_1\lambda_1;\mathbf{q}_2\lambda_2;\lambda'') \right) \\
&\times \left( \sum_{\lambda'''} v^{\alpha'}(\mathbf{q}\lambda\lambda'|\mathbf{q}_1\lambda_1';\mathbf{q}_2\lambda_2';\lambda''') \right)^*, \quad (59)
\end{aligned}$$

where

$$\begin{aligned}
v^\alpha(\mathbf{q}\lambda|\mathbf{q}_1\lambda_1;\mathbf{q}_2\lambda_2;\lambda'') &= u^\alpha(\mathbf{q}\lambda|\mathbf{q}_1\lambda'';\mathbf{q}_2\lambda_2) c_{\lambda''\lambda_1}(\mathbf{q}_1) \\
&+ u^\alpha(\mathbf{q}\lambda|\mathbf{q}_2\lambda'';\mathbf{q}_1\lambda_1) c_{\lambda''\lambda_2}(\mathbf{q}_2). \quad (60)
\end{aligned}$$

Neglecting the regular part  $[(\mathbf{J}^{-1}\mathbf{M}(\mathbf{q},t)\mathbf{J}^{-1})_{\lambda\lambda'}^{\alpha\alpha'}]_{\text{reg}}$ , Eqs. (43)–(45) and (58)–(60), together with Eqs. (40), (55), and (56), are closed-set equations for the density correlator  $S_{lm,l'm'}(\mathbf{q},t)$ , with the static correlators  $S_{lm,l'm'}(\mathbf{q})$  as input quantities.

Note that the vertices are neither positive nor real. Their behavior for  $\mathbf{q} \rightarrow \mathbf{0}$  is of interest. In Appendix D it will be proven that

$$\sum_{\lambda''} v^\alpha(\mathbf{q},\lambda|\mathbf{q}_1\lambda_1;\mathbf{q}_2\lambda_2;\lambda'') = \begin{cases} O(q), & \alpha=T, \lambda=(0,0) \\ O(1), & \text{otherwise} \end{cases} \quad (61)$$

implies

$$\begin{aligned}
V^{TT}(\mathbf{q},00,00|\mathbf{q}_1\lambda_1\lambda_1';\mathbf{q}_2\lambda_2\lambda_2') &= O(q^2), \\
V^{TR}(\mathbf{q},00,l'm'|\mathbf{q}_1\lambda_1\lambda_1';\mathbf{q}_2\lambda_2\lambda_2') &= O(q), \\
V^{RT}(\mathbf{q},lm,00|\mathbf{q}_1\lambda_1\lambda_1';\mathbf{q}_2\lambda_2\lambda_2') &= O(q), \quad (62)
\end{aligned}$$

and all others are equal to  $O(1)$ . This behavior relates to the fact that  $\mathbf{j}_{lm}^T(\mathbf{q})$ , in contrast to  $\mathbf{j}_{lm}^R(\mathbf{q})$ , is a conserved quantity for  $\mathbf{q} = \mathbf{0}$  and  $\lambda = (0,0)$ . For  $\lambda = \lambda' = \lambda_1 = \lambda_1' = \lambda_2 = \lambda_2' = (0,0)$  the vertex  $V^{TT}$  reduces to that for the simple liquid [1], as it should be.

Let us finally comment on the validity of the reduction theorem, which was proven for *simple* liquids by Götze [39]. The physical consequences of this theorem are probably the most important predictions of the MCT approach. It states that there exists a time scale  $t_\sigma(T)$  on which the  $\mathbf{q}$  and  $t$  dependences of the density correlator factorizes, and that its

$t$  dependence is given by a correlator  $G(t)$  which depends on the exponent parameter  $\lambda$  only.  $\lambda$  follows from the static correlator  $S(\mathbf{q})$  for  $T=T_c$ , i.e.,  $\lambda$  can be obtained from the microscopic information. The condition for the reduction theorem is that the bifurcation (of a glassy phase from the liquid) is of codimension 1. A sufficient condition for this is the positivity of the vertices. As can be seen from Eq. (59), this is not generally true for *molecular* liquids. However, in the diagonalization approximation, which will be used in Sec. IV, the vertices become real and positive. Despite the different structure of the MCT equations for  $l>0$  [cf. Eq. (78)], one can still prove that the reduction theorem is valid and that  $G(t)$  fulfills the same ‘‘universal’’ equation derived by Götze [39] for simple liquids. The only difference is that the microscopic calculation of  $\lambda$  also involves the static density correlators  $S_{lm,lm}(\mathbf{q})$  for  $l \geq 0$ .

#### IV. MCT FOR DIPOLAR HARD SPHERES

In this section we will apply the MCT equations which were derived in Sec. III to a system of dipolar hard spheres (DHS's). This system consists of hard spheres with diameter  $d$  and a dipolar moment  $\boldsymbol{\mu}$ . Besides the hard sphere interaction  $V_{\text{hs}}(\{\mathbf{x}_n\})$ , there is the dipolar interaction

$$V_{\text{dip}}(\{\mathbf{x}_n\}, \{\Omega_n\}) = \mu^2 \sum_{n \neq n'} |\mathbf{x}_n - \mathbf{x}_{n'}|^{-5} [(\mathbf{x}_n - \mathbf{x}_{n'})^2 (\mathbf{e}_n \mathbf{e}_{n'}) - 3((\mathbf{x}_n - \mathbf{x}_{n'}) \mathbf{e}_n)((\mathbf{x}_n - \mathbf{x}_{n'}) \mathbf{e}_{n'})], \quad (63)$$

where  $\mu = |\boldsymbol{\mu}|$  and  $\mathbf{e}_n = \boldsymbol{\mu}/\mu$ , the unit vector pointing in the direction of  $\Omega_n$ . We choose this system for two reasons. *First*, experimental results for  $S_q(t)$  for neutral colloidal systems, which can be well approximated by hard spheres, have shown a particularly good agreement with the predictions of the idealized version of the MCT [40,41]. Therefore, our MCT approach, which includes ODOF, may be a good approximation for DHS's, too. *Second*, for the direct correlation function  $c(\mathbf{x}, \Omega, \Omega')$  approximate, analytical expressions exist such that the input quantities of the MCT equations are known. Furthermore, the invariance of the potential under  $\boldsymbol{\mu}_n \rightarrow -\boldsymbol{\mu}_n$  for all  $n$  yields an additional restriction for  $S_{lm,l'm'}(\mathbf{q}, t)$ , which is

$$S_{lm,l'm'}(\mathbf{q}, t) = \begin{cases} 0, & l+l' \text{ odd} \\ \neq 0, & l+l' \text{ even.} \end{cases} \quad (64)$$

Let us now discuss  $c(\mathbf{x}, \Omega, \Omega')$ . Wertheim [42] showed that within the mean spherical approximation (MSA) (cf. also Ref. [34]) the calculation of  $c(\mathbf{x}, \Omega, \Omega')$  for dipolar hard spheres can be reduced to the case of simple hard sphere for which  $c(\mathbf{x})$  is known, e.g., in the Percus-Yevick approximation. Writing

$$c(\mathbf{x}, \Omega, \Omega') = c_s(r) + c_\Delta(r) \Delta(\mathbf{e}, \mathbf{e}') + c_D(r) D(\mathbf{e}_x, \mathbf{e}, \mathbf{e}'), \quad (65)$$

with

$$\Delta(\mathbf{e}, \mathbf{e}') = \mathbf{e} \cdot \mathbf{e}' \quad (66)$$

$$D(\mathbf{e}_x, \mathbf{e}, \mathbf{e}') = 3(\mathbf{e}_x \mathbf{e}^T)(\mathbf{e}_x \mathbf{e}'^T) - (\mathbf{e} \cdot \mathbf{e}'^T) \quad (67)$$

where  $r = |\mathbf{x}|$ ,  $\mathbf{e}_x = \mathbf{x}/r$  and  $\mathbf{e}, \mathbf{e}'$  are unit vectors pointing in the direction of  $\Omega, \Omega'$ , the  $r$ -dependent functions are given by [42]

$$c_s(r) = c_0(r; \varphi),$$

$$c_\Delta(r) = 2\kappa [c_0(r; 2\kappa\varphi) - c_0(r; -\kappa\varphi)], \quad (68)$$

$$c_D(r) = c_D^{(0)}(r) - 3r^{-3} \int_0^r dr' r'^2 c_D^{(0)}(r'),$$

where

$$c_D^{(0)}(r) = \kappa [2c_0(r; 2\kappa\varphi) + c_0(r; -\kappa\varphi)] \quad (69)$$

and the parameter  $\kappa = \kappa(T, \varphi)$  follows from

$$-c_0(2\kappa\varphi) + c_0(-\kappa\varphi) = 8\varphi\beta\mu^2/d^3. \quad (70)$$

Here the two control parameters *temperature*  $T(\beta = 1/kT)$  and the *packing fraction*  $\varphi = \pi\rho_0 d^3/6$  appear. The quantity  $\beta\mu^2/d^3 \equiv 1/T^*$  is the ratio of the characteristic dipolar energy  $\mu^2/d^3$  and the thermal energy. Hence  $T^*$  is a dimensionless temperature which is a measure of the dipolar energy for given  $T$ . The  $r$  dependence of  $c_0(r)$  in the Percus-Yevick approximation is given by [34]

$$c_0(r; \varphi) = \begin{cases} c_0(\varphi) + c_1(\varphi)(r/d) + c_3(\varphi)(r/d)^3, & r < d \\ 0, & r > d, \end{cases} \quad (71)$$

with

$$c_0(\varphi) = -(1 + 2\varphi)^2/(1 - \varphi)^4,$$

$$c_1(\varphi) = 6\varphi(1 + \varphi/2)^2/(1 - \varphi)^4,$$

$$c_3(\varphi) = \varphi c_0(\varphi)/2. \quad (72)$$

The calculation of

$$c_{lm;l'm'}(\mathbf{q}) = i^{l'-l} \int d^3x \int d^2\Omega \int d^2\Omega' c(\mathbf{x}, \Omega, \Omega') \times e^{-i\mathbf{q} \cdot \mathbf{x}} Y_{lm}^*(\Omega) Y_{l'm'}(\Omega') \quad (73)$$

is straightforward. As shown in Sec. II, it is convenient to use the  $q$  frame. The explicit expressions for  $c_{ll'}^m(q)$  are presented in Appendix E. From this appendix it follows that

$$c_{ll'}^m(q) = c_l^m(q) \delta_{ll'} \quad (74)$$

and  $c_l^m(q) \equiv 0$  for  $l \geq 2$ . Although this does not imply that the vertices vanish for  $l \geq 2$  and  $l' \geq 2$ , we will restrict the  $l$  values to 0 and 1. Due to this restriction and Eq. (64), the correlators become diagonal (in the  $q$  frame),

$$S_{ll'}^m(q, t) = S_l^m(q, t) \delta_{ll'}, \quad (75)$$

for  $l=0,1$  and  $l'=0,1$ . Consequently, only three independent correlators  $S_0^0(q, t)$ ,  $S_1^0(q, t)$  and  $S_1^1(q, t)$  exist. Because the inclusion of ODOF's has made the MCT equations much

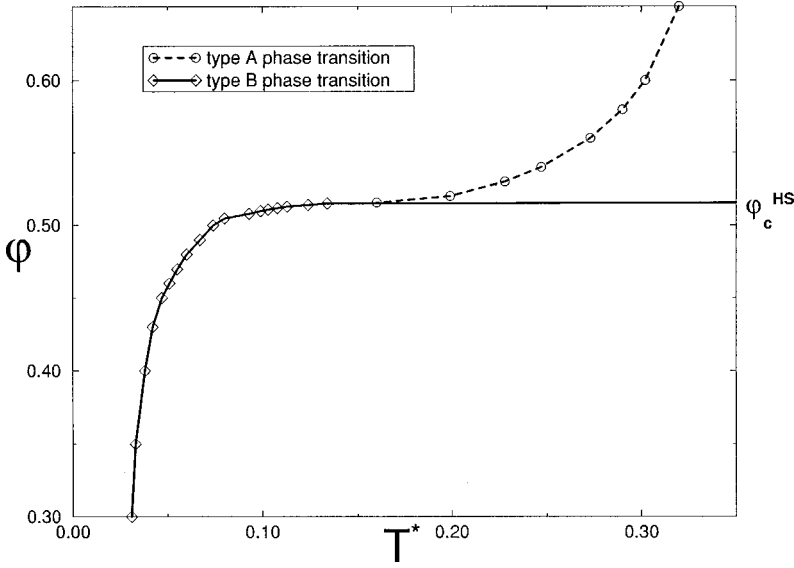


FIG. 1. The phase diagram for the liquid and glassy phases of a system of dipolar hard spheres.  $\varphi$  and  $T^*$  denote the packing fraction and the reduced temperature  $T^* = kTd^3/\mu^2$ , respectively.

more involved compared to simple liquids, we think that this restriction is a reasonable starting point.

We will restrict the discussion of the MCT equations to the nonergodicity parameter

$$f_l^m(q) = \lim_{t \rightarrow \infty} S_l^m(q, t) / S_l^m(q). \quad (76)$$

For this the memory kernel  $\mathbf{M}(\mathbf{q}, t)$  is also transformed to the  $q$  frame. Then,  $f_l^m(q)$  is the solution of

$$\frac{f_0^m(q)}{1 - f_0^m(q)} = (\mathcal{F}^T)_0^m(q; \{f_l^m\}) \quad (77)$$

and

$$\frac{f_1^m}{1 - f_1^m} = \left[ \frac{1}{(\mathcal{F}^T)_1^m(q; \{f_l^m\})} + \frac{1}{(\mathcal{F}^R)_1^m(q; \{f_l^m\})} \right]^{-1} \quad (78)$$

for  $m=0$  and 1. Here we performed one more *approximation* which is the diagonalization of the memory kernel with respect to  $\alpha$  and  $\alpha'$ . Due to this, the vertices become *real* and *non-negative*. The reader should not confuse the superscript  $T$  with temperature. The functionals  $(\mathcal{F}^\alpha)_l^m(q; \{f_l^m\})$  follow from  $m_{lm; l'm'}^{\alpha\alpha'}(\mathbf{q}, t)$  after transformation to the  $q$  frame, and are of the form

$$(\mathcal{F}^\alpha)_l^m(q; \{f_l^m\}) = \int_0^\infty dq_1 \int_{|q-q_1|}^{q+q_1} dq_2 (\mathcal{K}^\alpha)_l^m(q, q_1, q_2; \{f_l^m\}),$$

with

$$\begin{aligned} (\mathcal{K}^T)_0^m(q, q_1, q_2; \{f_l^m\}) &= (V_{00,00}^T)_0^m(q, q_1, q_2) f_0^m(q_1) f_0^m(q_2) \\ &+ (V_{11,10}^T)_0^m(q, q_1, q_2) [f_1^m(q_1) f_1^m(q_2) \\ &+ f_1^m(q_2) f_1^m(q_1)] \\ &+ (V_{10,10}^T)_0^m(q, q_1, q_2) f_1^m(q_1) f_1^m(q_2) \\ &+ (V_{11,11}^T)_0^m(q, q_1, q_2) f_1^m(q_1) f_1^m(q_2) \end{aligned} \quad (79)$$

and

$$\begin{aligned} (\mathcal{K}^\alpha)_1^m(q, q_1, q_2; \{f_l^m\}) &= (V_{00,10}^\alpha)_1^m(q, q_1, q_2) [f_0^m(q_1) f_1^m(q_2) \\ &+ f_0^m(q_2) f_1^m(q_1)] \\ &+ (V_{00,11}^\alpha)_1^m(q, q_1, q_2) [f_0^m(q_1) f_1^m(q_2) \\ &+ f_0^m(q_2) f_1^m(q_1)]. \end{aligned} \quad (80)$$

The reduced vertices  $(V_{l_1 m_1, l_2 m_2}^\alpha)_l^m$  are obtained from Eqs. (59), (60), (55), and (56). We do not present them explicitly, but discuss qualitatively their  $\varphi$  and  $T$  dependence. For this it is important to notice that  $(V_{l_1 m_1, l_2 m_2}^\alpha)_l^m$  involves  $c_{l_1}^{m_1}(q_1) c_{l_2}^{m_2}(q_2)$ . Fixing  $\varphi (0 < \varphi < 1)$  one finds from Eqs. (68)–(73) that

$$c_0^0(q; \varphi, T) \rightarrow c_0^0(q; \varphi) \neq 0, \quad (81)$$

$$c_1^m(q; \varphi, T) \rightarrow 0$$

for  $T$  (or  $T^*) \rightarrow \infty$ . Therefore, for  $T = \infty$  the functional  $(\mathcal{F}^T)_0^m$  reduces to that for simple hard spheres, as is expected. In this case there is a dynamic transition (type B) at a critical packing fraction  $\varphi_c \approx 0.51$ – $0.52$  [43–45] such that  $f(q) \equiv f_0^0(q) > 0$  for  $\varphi \geq \varphi_c$ , and  $f_1^m(q) \equiv 0$  otherwise.

To determine the phase diagram we have solved numerically Eqs. (77)–(80) for given  $\varphi$  and  $T$ . Figure 1 represents the result. There are two phase boundaries where a type-B transition (solid line) and a type-A transition (dashed line) take place, respectively. Three different transition scenarios are possible: for  $T_1^* \approx 0.32 < T^* \leq \infty$  the TDOF freeze at  $\varphi_c \approx 0.52$  into a nonergodic phase (type B), whereas the ODOF remains ergodic for all  $\varphi$ . Note that  $T_1^*$  is the value on the type-A transition line for  $\varphi_{\text{RCP}} = 0.64$ , the packing fraction for random close packing. Since larger values than  $\varphi_{\text{RCP}}$  are unphysical, we have used  $\varphi_{\text{RCP}}$  as a cutoff. In addition we stress that the accuracy of  $T_1^*$  should not be overestimated,



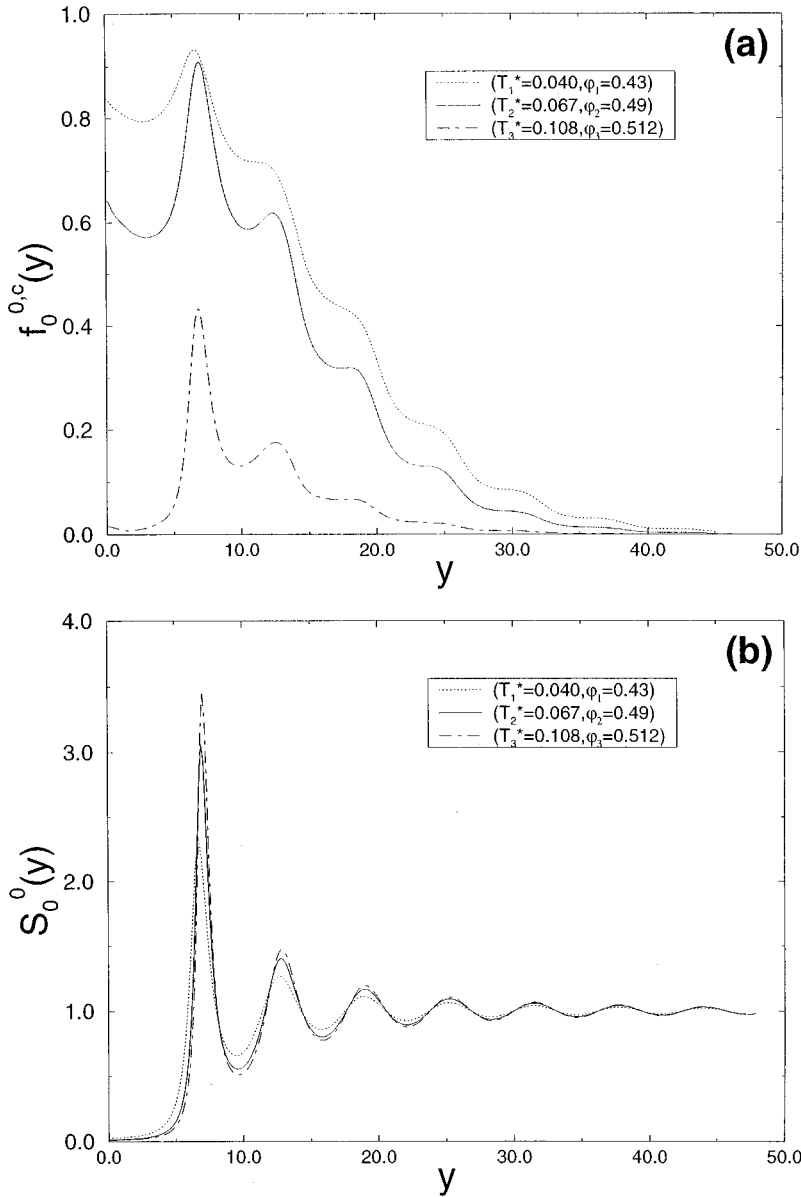


FIG. 2. The critical nonergodicity parameter (a) and the static correlator (b) for  $l=0$ ,  $m=0$  and three different points for  $(T^*, \varphi)$  on the critical line  $\varphi_c^B(T)$  as a function of  $y=qd$ .

because the Percus-Yevick approximation for hard spheres does not describe correctly the singularity which is expected for  $\varphi = \varphi_{\text{RCP}}$ . Hence this approximation becomes worse by “approaching  $\varphi_{\text{RCP}}$ . If  $T_2^* \approx 0.13 \leq T^* \leq T_1^*$ , the same happens for the TDOF as before, but by a further increase of  $\varphi$  the ODOF freeze via a type-A transition at the critical line  $\varphi_c^A(T)$  (dashed line). Since the determination of the location of the critical line was rather computer time consuming, we were not able to locate  $T_2^*$  better than about 10% due to the flatness of the critical lines in the vicinity of  $T_2^*$ . For  $T^* < T_2^*$ , both TDOF’s and ODOF’s freeze simultaneously at the critical line  $\varphi_c^B(T)$  (type B) (solid line for  $T^* < T_2^*$ ).

Figures 2(a), 3(a), and 4(a) represent the critical nonergodicity parameters  $f_l^{m,c}(y)$ , and Figs. 2(b), 3(b), and 4(b), corresponding static correlators  $S_l^m(y)$  for three different points on  $\varphi_c^B(T)$  for  $T^* < T_2^*$ . Comparison of both sets of figures shows that the  $q$  dependence ( $y$  dependence) of  $f_l^{m,c}$  is in phase with the  $q$  dependence of  $S_l^m$ . Hence we find a similar behavior for  $(l,m) \neq (0,0)$  as already found for

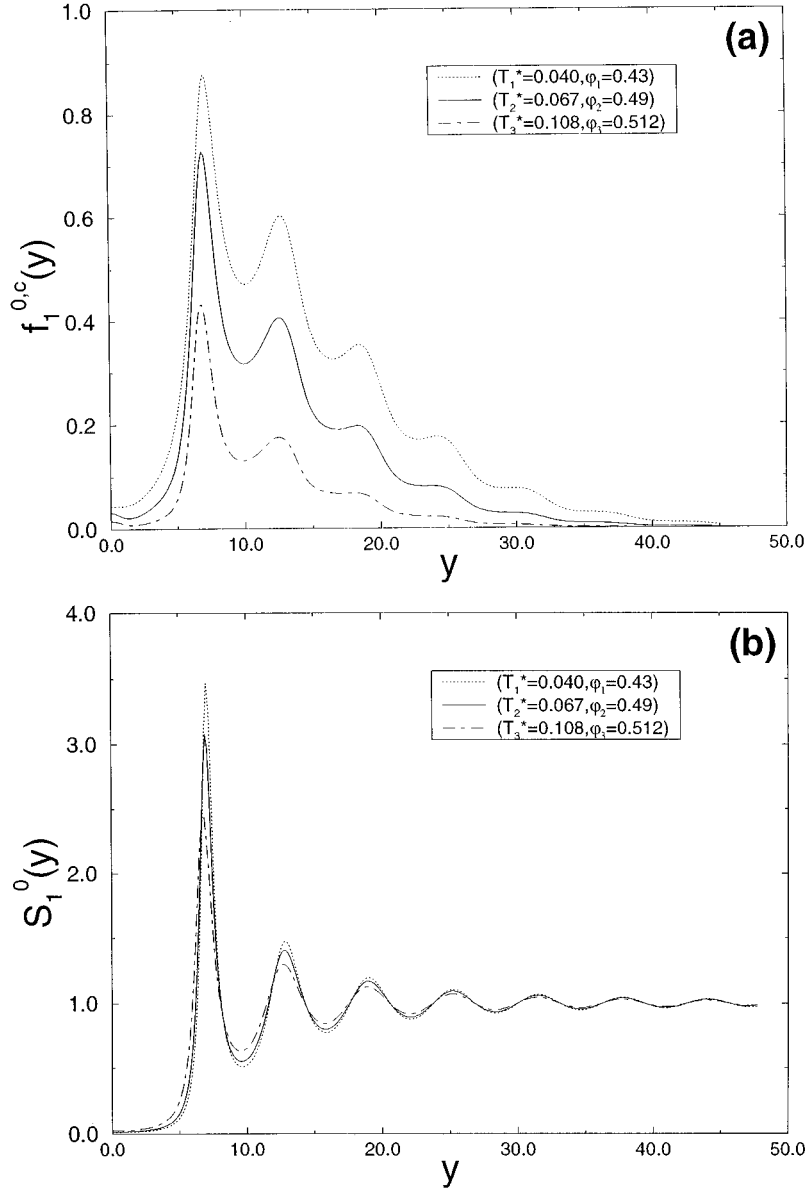
simple liquids, i.e., for  $(l,m) = (0,0)$  [1]. Furthermore, we point out the strong  $m$  dependence of  $f_l^{m,c}(y)$ , even for  $y = 0$ . Since the form factors  $f_l^{m,c}(y)$  increase uniformly when moving on  $\varphi_c^B(T)$  toward  $T \rightarrow 0$ , the TDOF’s and ODOF’s become more arrested in that case.

In dielectric spectroscopy information on the rotationally invariant correlator

$$S_1(q,t) = \sum_{m=-1}^1 S_1^m(q,t) \quad (82)$$

for  $q=0$  is obtained. The corresponding nonergodicity parameter  $f_1(q)$  follows from

$$f_1(q) = \lim_{t \rightarrow \infty} \frac{\sum_{m=-1}^1 S_1^m(q,t)}{\sum_{m=-1}^1 S_1^m(q)}. \quad (83)$$

FIG. 3. Same as Fig. 2, but for  $l=1, m=0$ .

$f_1^c(q)$  is presented in Fig. 5 for three different points on  $\varphi_c^B(T)$  for  $T^* < T_2^*$ .  $f_1^c(q)$  gives the strength of the  $\alpha$  relaxation for  $T > T_c(\varphi)$  ( $\varphi$  fixed), i.e., the area under the  $\alpha$  peak of the imaginary part  $\chi_{l=1}^{(0)''}(q, \omega)$  of the corresponding susceptibility  $\chi_{l=1}^{(0)}(q, \omega)$  as a function of  $\ln \omega$  is  $f_1^c(q)$  [1]. The superscript (0) indicates the susceptibility (for  $l=1$ ) with respect to the *external* electric field. Therefore,  $1 - f_1^c(q)$  is a measure for the remaining spectrum (minimum and microscopic or Boson peak) due to a sum rule [1]. Since  $1 - f_1^c(q)$  is rather small compared to  $1 - f_0^c(q)$  for  $q=0$  (at least for the two lowest temperatures shown in Fig. 5) the minimum between the  $\alpha$  peak and the microscopic or Boson peak might be rather shallow for  $\chi_{l=1}^{(0)''}(0, \omega)$  compared to  $\chi_{l=0}^{(0)''}(0, \omega)$  (see also the discussion of that point in Sec. V).

In contrast to  $\chi_{l=1}^{(0)}(q=0, \omega)$ , it is the dielectric function  $\varepsilon(q=0, \omega)$  which is directly accessible in a dielectric experiment. Its (normalized) imaginary part  $\varepsilon''(q=0, \omega) \equiv \varepsilon''(\omega)$  is given by [33,46]:

$$\varepsilon''(\omega) = \lim_{q \rightarrow 0} \chi_{11}^{(0)''}(q\mathbf{e}_3, \omega) = \lim_{q \rightarrow 0} \chi_{22}^{(0)''}(q\mathbf{e}_3, \omega), \quad (84)$$

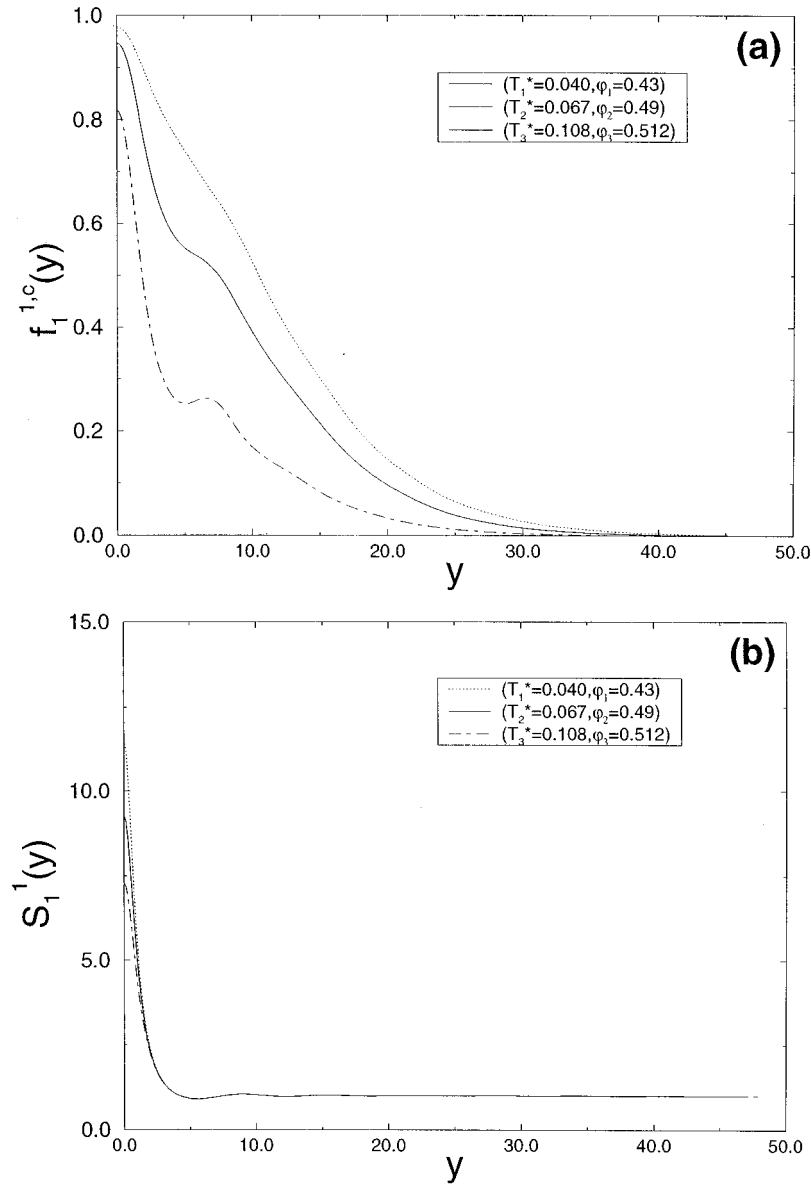
where  $(\chi_{ij}^{(0)}(q, \omega))(i, j=1, 2, 3)$  is the (Cartesian) susceptibility tensor (normalized with respect to the static susceptibility). Due to the long-range character of the dipolar interactions it is

$$\lim_{q \rightarrow 0} \chi_{33}^{(0)''}(q\mathbf{e}_3, \omega) \neq \lim_{q \rightarrow 0} \chi_{11}^{(0)''}(q\mathbf{e}_3, \omega). \quad (85)$$

Making use of the fluctuation dissipation theorem and the relationship between  $\chi_{ij}^{(0)}$  and  $(\chi^{(0)})_1^m$ , one obtains

$$\varepsilon''(\omega) = (\chi^{(0)})_1^{(0)''}(q=0, \omega) = \frac{1}{2} \omega \lim_{q \rightarrow 0} \widetilde{S}_1^1(q, \omega) / S_1^1(q), \quad (86)$$

where  $\widetilde{S}_l^m(q, \omega)$  is the Fourier transform of  $S_l^m(q, t)$ , and  $(\chi^{(0)})_l^{(0)''}(q, \omega)$  the imaginary part of the corresponding (normalized) susceptibility.

FIG. 4. Same as Fig. 2, but for  $l=1$ ,  $m=1$ .

The reader should note that inequality (85) implies that  $\bar{S}_1^m(0, \omega)$  and therefore  $S_1^m(0, t)$ , too, depends on  $m$ . This can be observed for  $t=0$  from Figs. 3(b) and 4(b) and can be proven with the explicit result for  $c_l^m(q)$  in Appendix E. A similar relationship to Eq. (86) holds for the imaginary part  $\kappa''(q\mathbf{e}_3, \omega)$  of the compressibility

$$\kappa''(q\mathbf{e}_3, \omega) = \chi_0''(q\mathbf{e}_3, \omega) = \frac{1}{2} \omega \bar{S}_0^0(q, \omega) / S_0^0(q). \quad (87)$$

Again, the area under the  $\alpha$  peak of  $\chi_l^{m''}(q\mathbf{e}_3, \omega)$  as a function of  $\ln \omega$  is about  $f_l^{m,c}(q)$ . From Figs. 2(a) and 4(a) we obtain

$$f_1^{1,c}(q=0) > f_0^{0,c}(q=q_1) \geq f_0^{0,c}(q) \quad (88)$$

for the three points on the critical line  $\eta_c^B(T)$ .  $q_1$  is the position of the first maximum of  $S_0^0(q)$ . For instance, it is  $f_1^{1,c}(q=0) \approx 2 f_0^{0,c}(q=q_1)$  for the point with highest temperature. Therefore, the strength of the  $\alpha$  process (normalized to the static susceptibility) obtained from the dielectric

measurement (which is at  $q=0$ !) is about twice as large as that which will follow from neutron scattering at  $q=q_1$ .

## V. DISCUSSION AND CONCLUSIONS

In this paper we presented a generalization of the mode coupling description of the ideal glass transition in simple liquids to molecular liquids. We considered linear molecules only. The extension to arbitrary molecules is straightforward [47].

We demonstrated that the choice of  $j_{lm}^T(\mathbf{q})$  and  $j_{lm}^R(\mathbf{q})$ , besides  $\delta\rho_{lm}(\mathbf{q})$ , as slow variables is necessary in order to avoid inertia effects for the long time dynamics (cf. Ref. [25]). With the type of approximation we performed for the static three-point correlator, one ends up with expressions for the vertices of the mode coupling polynomial which are in a close relationship to those for simple liquids [1–3].

The resulting MCT equations for the nonergodicity parameter were solved for a system of dipolar hard spheres. Making use of the static correlators in mean spherical and

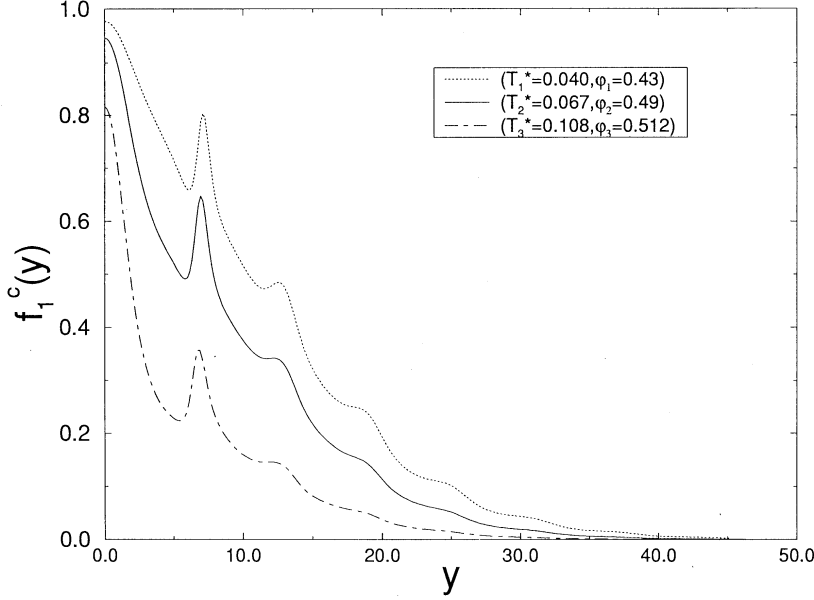


FIG. 5. The rotational invariant non-ergodicity parameter  $f_1^c$  for the same  $(T^*, \varphi)$  values as in Fig. 2 as a function of  $y = qd$ .

Percus-Yevick approximation, and restricting to  $l=0,1$ , the  $\varphi$ - $T$  phase diagram was determined. For this we have also assumed diagonality of the memory kernel with respect to  $\alpha$  and  $\alpha'$ . Taking also  $m_{\lambda\lambda}^{RT}(q,t)$  into account, does not change the topology of the phase diagram, but shifts the phase boundaries toward higher temperatures [47]. The main conclusion which can be drawn is the existence of three different transition scenarios, as follows.

(i) Only the TDOF's freeze, whereas the ODOF's remain "liquid." This happens for all  $\varphi$  with  $\varphi_c \cong 0.52 \leq \varphi < \varphi_{\text{RCF}}$ , provided  $T_1 < T \leq \infty$ . In this temperature range there is *no* influence of the dipolar interactions. The nonergodicity parameter  $f_0^0(q; \varphi, T)$  is  $T$  independent, and its  $q$  and  $\varphi$  dependences are identical to that for the hard sphere system, without dipoles.

(ii) If  $T_2 \leq T \leq T_1$ , the TDOF's freeze first at  $\varphi_c \cong 0.52$  via a type-B transition, and at the critical line  $\varphi_c^A(T)$  (the dashed line in Fig. 1) the ODOF's freeze by a type-A transition. This latter transition corresponds to a *spin glass transition* [48], as was discussed within MCT for Heisenberg spin glasses by Götz and Sjögren [49].

(iii) For  $T < T_2$ , both TDOF's and ODOF's freeze simultaneously at the critical line  $\varphi_c^B(T)$ . These findings demonstrate a hierarchy for the freezing, i.e., the ODOF's can never freeze before the TDOF's are frozen. This result becomes obvious from Eq. (80). Assuming  $f_0^0(q) \equiv 0$ , it follows that  $(\mathcal{H}^\alpha)_1^m \equiv 0$ , which implies that  $f_1^m(q) \equiv 0$ . A freezing of the ODOF's alone, could only occur if  $(\mathcal{K}^\alpha)_1^m$  would involve a term  $f_1^m(q_1)f_1^m(q_2)$ . Such a term, however, is forbidden due to the parity rule which requires  $l+l_1+l_2$  to be *even*. We stress that the topology of the phase diagram (cf. Fig. 1) and in particular the existence of a type-A transition is neither an artifact of the restriction of  $l$  to 0 and 1 nor an artifact of the approximation of the static three-point correlator [cf. Eq. (C6)], but a result of the additional symmetry of dipolar hard spheres, which is the invariance under the transformation  $\{\boldsymbol{\mu}_n\} \rightarrow \{-\boldsymbol{\mu}_n\}$ . This symmetry implies that  $S_{lm,l'm'}(\mathbf{q}, \mathbf{t})$ , and therefore  $f_{lm,l'm'}(\mathbf{q})$  and  $M_{lm,l'm'}^{\alpha\alpha'}(\mathbf{q}, \mathbf{t})$ , vanish if  $l+l'$

is odd. Consequently,  $l$  and  $l'$  must be both either even or odd. Let us symbolically denote  $f_{lm,l'm'}(\mathbf{q})$  by  $f_{\text{even}}(\mathbf{q})$  and  $f_{\text{odd}}(\mathbf{q})$  for  $l, l'$  even and  $l, l'$  odd, respectively, and similarly for  $M_{lm,l'm'}^{\alpha\alpha'}(\mathbf{q}, \mathbf{t})$ . Then the equation for  $f_{\text{even}}$  involves  $M_{\text{even}}^{\alpha\alpha'}$  and that for  $f_{\text{odd}}$  involves  $M_{\text{odd}}^{\alpha\alpha'}$  only. Taking further into account that the vertices of  $M_{lm,l'm'}^{\alpha\alpha'}$  vanish for  $l+l_1+l_2$  odd and/or  $l'+l'_1+l'_2$  odd [cf. Eq. (53)], due to the additional symmetry, it is easy to prove that  $M_{\text{even}}^{\alpha\alpha'}$  [Eq. (53)] only contains bilinear terms  $f_{\text{even}}(\mathbf{q}_1)f_{\text{even}}(\mathbf{q}_2)$  and  $f_{\text{odd}}(\mathbf{q}_1)f_{\text{odd}}(\mathbf{q}_2)$ , whereas  $M_{\text{odd}}^{\alpha\alpha'}$  only involves  $[f_{\text{even}}(\mathbf{q}_1)f_{\text{odd}}(\mathbf{q}_2) + (1 \leftrightarrow 2)]$ , but *no* terms  $f_{\text{odd}}(\mathbf{q}_1)f_{\text{odd}}(\mathbf{q}_2)$  and  $f_{\text{even}}(\mathbf{q}_1)f_{\text{even}}(\mathbf{q}_2)$ . It is the absence of these two latter terms which allows for the existence of a type-A transition for  $f_{\text{odd}}$ . This result is in agreement with a rather general treatment of a bilinear memory kernel, where it has been proven that a type-A transition can only occur if an additional symmetry exists [50]. The structure of  $M_{\text{even}}^{\alpha\alpha'}$  and of  $M_{\text{odd}}^{\alpha\alpha'}$  also implies that a freezing of the TDOF's (i.e.,  $l=l'=0$ ) induces a glass transition for all  $f_{lm,l'm'}$  with  $l$  and  $l'$  even. This can happen already at arbitrary high temperatures, provided  $\varphi > \varphi_c$ . Similarly, if  $f_{l_o, l'_o, m'}$  for  $l_o, l'_o$  odd freezes, then all ODOF's with  $l$  and  $l'$  odd will freeze. Therefore, the different transition scenarios described above do not really discriminate between TDOF's and ODOF's, but between  $l, l'$  even and  $l, l'$  odd.

This hierarchy of freezing also points out the different role of packing and temperature. Primarily, it is the *dense packing* which leads to the *cage effect* [1] and finally to the freezing of the TDOF's. The temperature (as far as the density remains constant) seems to play a less important role.

With the behavior of the static correlators for  $\varphi \rightarrow 0$  and  $T \rightarrow 0$ , one can prove that the critical line  $\varphi_c^B(T)$  does *not* go to zero at a *finite* temperature below  $T_2$ . Although an extrapolation of the steep descent of  $\varphi_c^B(T)$  depicted in Fig. 1 would suggest the existence of such a finite temperature, one can prove that  $\varphi_c^B(T) \rightarrow 0$  for  $T \rightarrow 0$ . In this respect we would

like to mention that a similar steep descent of  $\varphi_c^B(T)$  has been found by Lai and Chang [51] for a system of *charged* hard spheres.

The variation of the nonergodicity parameters  $f_1^{m,c}(q)$  (on the critical type-B line) in phase with  $S_1^m(q)$  is similar to the behavior found for simple liquids [1]. Comparison of Figs. 2(a) and 4(a) shows that  $f_1^{1,c}(q=0) > f_0^{0,c}(q=q_1) \geq f_0^{0,c}(q)$  for the three different points on the critical line  $\varphi_c^B(T)$  we investigated. This implies that the spectral weight of the ‘‘normalized’’  $\alpha$  peak obtained from a macroscopic (i.e.,  $q=0$ ), dielectric measurement is larger than that from neutron scattering for arbitrary  $q$ , at least for these points on  $\varphi_c^B(T)$ . The reason for this behavior is as follows: comparison of Figs. 2(b) and 4(b) reveals that the *static* correlator  $S_1^1(q)$  is rather structureless, with a well-pronounced maximum at  $q=0$ , whereas  $S_0^0(q)$  possesses the typical variation with  $q$ , as known for liquids. It is the fact that  $S_1^1(q=0)$  is significantly larger than  $S_0^0(q)$  for all  $q$ , which makes  $f_1^{1,c}(q=0)$  larger than  $f_0^{0,c}(q)$ . From this, one might conclude that the minimum between the  $\alpha$  peak and the microscopic (or Boson peak) will be less pronounced for dielectric data than for that from neutron scattering (due to a sum rule [1]), provided the spectral line width of the microscopic (or Boson peak) is about the same in both cases. We are aware that this argument is rather crude. A quantitative investigation of this question will require a solution of the time-dependent MCT equations including the microscopic frequencies, as it was done recently for a schematic model [52]. Let us finally mention that the static correlator  $S_1^1(q)$  for a liquid of rigid diatomic molecules with Lennard-Jones interactions (without dipolar interactions) does not exhibit a maximum at  $q=0$  [32] as it is the case for DHS’s. This may stress the importance of the dipolar interactions for the conclusions with respect to the relaxation strength of the  $\alpha$  peak obtained from dielectric spectroscopy.

Since neither experimental nor numerical data are available for the dynamics of dipolar hard spheres, it is not possible to check the validity of our results. Therefore, it will be important to investigate our MCT equations for systems where this information is known.

#### ACKNOWLEDGMENTS

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#### APPENDIX A: CALCULATION OF $J_{\lambda_1\lambda_2}^{\alpha_1\alpha_2}(\mathbf{q})$

In this and the following appendixes we will present technical details of our calculations. The crucial steps will be given only. For Eq. (40), with Eqs. (17), (22), (36), and (37), we obtain

$$J_{\lambda_1\lambda_2}^{\alpha_1\alpha_2}(\mathbf{q}) = \frac{1}{N} (q_{l_1}^{\alpha_1}(\mathbf{q}) q_{l_2}^{\alpha_2}(\mathbf{q}))^{-1} \\ \times \sum_{n_1 n_2} \sum_{k_1 k_2} \langle v_{n_1}^{\alpha_1 k_1} (\hat{q}^{\alpha_1 k_1} \rho_{n_1})_{\lambda_1}(\mathbf{q})^* \\ \times v_{n_2}^{\alpha_2 k_2} (\hat{q}^{\alpha_2 k_2} \rho_{n_2})_{\lambda_2}(\mathbf{q}) \rangle, \quad (\text{A1})$$

where we introduced

$$\rho_{n,\lambda}(\mathbf{q}) = \sqrt{4\pi} i^l e^{i\mathbf{q}\cdot\mathbf{x}_n} Y_{lm}(\Omega_n), \quad \lambda = (l, m). \quad (\text{A2})$$

Since

$$\langle v_{n_1}^{\alpha_1 k_1} v_{n_2}^{\alpha_2 k_2} \dots \rangle = \langle v_{n_1}^{\alpha_1 k_1} v_{n_2}^{\alpha_2 k_2} \rangle \langle \dots \rangle \\ = \frac{kT}{I_{\alpha_1}} \delta_{\alpha_1\alpha_2} \delta_{k_1 k_2} \delta_{n_1 n_2} \langle \dots \rangle, \quad (\text{A3})$$

it follows that

$$J_{\lambda_1\lambda_2}^{\alpha_1\alpha_2}(\mathbf{q}) = \frac{1}{N} (q_{l_1}^{\alpha_1}(\mathbf{q}) q_{l_2}^{\alpha_2}(\mathbf{q}))^{-1} \delta_{\alpha_1\alpha_2} \frac{kT}{I_{\alpha_1}} \\ \times \sum_n \langle (\hat{q}^{\alpha_1} \rho_n)_{\lambda_1}(\mathbf{q})^* (\hat{q}^{\alpha_1} \rho_n)_{\lambda_2}(\mathbf{q}) \rangle. \quad (\text{A4})$$

Here a comment is in order. To derive Eq. (A3) for  $\alpha_1 = \alpha_2 = R$  it is important to use the angular velocity  $\boldsymbol{\omega}'_n$  and the angular momentum operator  $\mathbf{L}'$  in the body fixed frame [where  $L'_3 = (R(\phi, \theta)L)_3 = 0$ ] because only then  $\exp(-\beta H)$  factorizes into a kinetic and a potential part where the kinetic term only involves  $\boldsymbol{\omega}'_n$  [34]. After having performed the averaging over  $\{\boldsymbol{\omega}'_n\}$  one may transform back to the laboratory fixed frame. For  $\alpha = T$  and  $\alpha' = R$ , or vice versa, it is obvious that the correlator must vanish, since  $\langle v_{n_1}^{Tk_1} v_{n_2}^{Rk_2} \dots \rangle = \langle v_{n_1}^{Tk_1} \rangle \langle v_{n_2}^{Rk_2} \rangle \langle \dots \rangle = 0$ , due to  $\langle v_{n_1}^{Tk_1} \rangle = 0$ .

Next, we notice that  $(\hat{\mathbf{q}}^\alpha \rho_n)_{\lambda_1}(\mathbf{q}_1)^* (\hat{\mathbf{q}}^\alpha \rho_n)_{\lambda_2}(\mathbf{q}_2)$  transforms under  $R \in O(3)$  like

$$\exp[-i(\mathbf{q}_1 - \mathbf{q}_2)\mathbf{x}_n] Y_{l_1 m_1}^*(\Omega_n) Y_{l_2 m_2}(\Omega_n) \\ = \exp[-i(\mathbf{q}_1 - \mathbf{q}_2)\mathbf{x}_n] (-1)^{m_1} Y_{l_1 -m_1}(\Omega_n) Y_{l_2 m_2}(\Omega_n).$$

Therefore, it is

$$(\hat{\mathbf{q}}^\alpha \rho_n)_{\lambda_1}(\mathbf{q}_1)^* (\hat{\mathbf{q}}^\alpha \rho_n)_{\lambda_2}(\mathbf{q}_2) \\ = (-1)^{m_1} \sum_\lambda C(l_1 l_2 l; -m_1 m_2 m) a_{l_1 l_2 l}^\alpha(\mathbf{q}_1 \mathbf{q}_2) \\ \times \sqrt{4\pi} (-i)^l e^{-i(\mathbf{q}_1 - \mathbf{q}_2)\cdot\mathbf{x}_n} Y_{lm}(\Omega_n) \\ = (-1)^{m_2} \sum_\lambda C(l_1 l_2 l; -m_1 m_2 m) a_{l_1 l_2 l}^\alpha(\mathbf{q}_1 \mathbf{q}_2) \\ \times \rho_{n,\lambda}^*(\mathbf{q}_1 - \mathbf{q}_2), \quad (\text{A5})$$

where  $a_{l_1 l_2 l}^\alpha(\mathbf{q}_1 \mathbf{q}_2)$ , which depends on  $l_1$ ,  $l_2$ ,  $l$  and  $(\mathbf{q}_1 \cdot \mathbf{q}_2)$  only, takes into account that the left-hand side of Eq. (A5) is not normalized. With the scalar product

$$\begin{aligned} \langle \rho_{n,\lambda}(\mathbf{q}), \rho_{n,\lambda'}(\mathbf{q}') \rangle &= \frac{1}{4\pi V} \int_V d^3 x_n \int d^2 \Omega_n \\ &\quad \times \rho_{n,\lambda}(\mathbf{q})^* \rho_{n,\lambda'}(\mathbf{q}') \\ &= \delta_{\mathbf{q},\mathbf{q}'} \delta_{\lambda,\lambda'}, \end{aligned} \quad (\text{A6})$$

we immediately obtain, from Eq. (A5),

$$\begin{aligned} a_{l_1 l_2 l}^\alpha(\mathbf{q}_1 \mathbf{q}_2) &= (C(l_1 l_2 l; 000))^{-1} ((\hat{\mathbf{q}}^\alpha \rho_n)_{l_1 0}(\mathbf{q}_1) \\ &\quad \times (\hat{\mathbf{q}}^\alpha \rho_n)_{l_2 0}(\mathbf{q}_2)^* \rho_{n,l_0}(\mathbf{q}_1 - \mathbf{q}_2)), \end{aligned} \quad (\text{A7})$$

where a straightforward calculation, which uses the product rule for  $Y_{lm}$  [34], yields, with Eqs. (22), (A2), and (A6),

$$a_{l_1 l_2 l}^\alpha(\mathbf{q}_1 \mathbf{q}_2) = i^{l+l_2-l_1} \left( \frac{(2l_1+1)(2l_2+1)}{2l+1} \right)^{1/2} \begin{cases} \mathbf{q}_1 \mathbf{q}_2 C(l_1 l_2 l; 000), & \alpha = T \\ (l_1(l_1+1)l_2(l_2+1))^{1/2} (-\frac{1}{2}) [C(l_1 l_2 l; 1-10) + C(l_1 l_2 l; 110)], & \alpha = R. \end{cases} \quad (\text{A8})$$

Equation (A5) together with Eq. (A8) is the basic result, which will be used in the following. Since it is

$$\langle \rho_{n,\lambda}(\mathbf{q}) \rangle = \delta_{q,0} \delta_{\lambda,0}, \quad (\text{A9})$$

with Eqs. (A5), (A8) and  $C(l_1 l_2 0; m_1 m_2 0)$  from Ref. [34] we obtain that

$$\langle (\hat{\mathbf{q}}^{\alpha_1} \rho_n)_{\lambda_1}(\mathbf{q})^* (\hat{\mathbf{q}}^{\alpha_2} \rho_n)_{\lambda_2}(\mathbf{q}) \rangle = \delta_{\lambda_1, \lambda_2} (q_{l_1}^{\alpha_1}(\mathbf{q}))^2, \quad (\text{A10})$$

with  $q_l^\alpha(\mathbf{q})$  from Eq. (37). Substituting Eq. (A10) into Eq. (A4) finally yields

$$J_{\lambda_1 \lambda_2}^{\alpha_1 \alpha_2}(\mathbf{q}) = \frac{kT}{I_{\alpha_1}} \delta_{\lambda_1, \lambda_2} \delta_{\alpha_1, \alpha_2} \quad (\text{A11})$$

for all  $\mathbf{q}$ .

## APPENDIX B: CALCULATION OF

$$\langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* \mathcal{Q} | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle$$

Substitution of  $\mathcal{Q} = 1 - P$  leads to

$$\begin{aligned} &\langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* \mathcal{Q} | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= \langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &\quad - \langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* P | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle, \end{aligned} \quad (\text{B1})$$

(i) Let us first calculate  $\langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle$ . Because  $\mathcal{L}$  is Hermitian, it is

$$\begin{aligned} &\langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= \langle j_\lambda^\alpha(\mathbf{q})^* | (\mathcal{L} \delta \rho_{\lambda_1}(\mathbf{q}_1)) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle + (1 \leftrightarrow 2) \\ &= (q_l^\alpha(\mathbf{q}))^{-1} \sum_{\alpha_1} \langle (\hat{\mathbf{q}}^{\alpha_1} \mathbf{j}^\alpha)_\lambda(\mathbf{q})^* (\hat{\mathbf{q}}^{\alpha_1} \mathbf{j}^{\alpha_1})_{\lambda_1}(\mathbf{q}_1) \\ &\quad \times \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle + (1 \leftrightarrow 2), \end{aligned} \quad (\text{B2})$$

where Eqs. (20) and (36) were used. Substituting  $j_\lambda^\alpha(\mathbf{q})$  from Eq. (17) into Eq. (B2), and performing the average over the velocities (cf. Appendix A) with Eq. (A2) we obtain

$$\begin{aligned} &\langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= \frac{kT}{I_\alpha} (q_l^\alpha(\mathbf{q}))^{-1} \sum_n \langle (\hat{\mathbf{q}}^\alpha \rho_n)_\lambda(\mathbf{q})^* (\hat{\mathbf{q}}^\alpha \rho_n)_{\lambda_1}(\mathbf{q}_1) \\ &\quad \times \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle + (1 \leftrightarrow 2). \end{aligned} \quad (\text{B3})$$

Now, Eq. (A5) can be used. This yields

$$\begin{aligned} &\langle \mathcal{L} j_\lambda^\alpha(\mathbf{q})^* | \delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= \frac{kT}{I_\alpha} (q_l^\alpha(\mathbf{q}))^{-1} (-1)^{m_1} \sum_{\lambda_2''} C(ll_1 l_2''; -mm_1 - m_2'') \\ &\quad \times a_{ll_1 l_2''}^\alpha(\mathbf{q} \cdot \mathbf{q}_1) \left\langle \sum_n \rho_{n,\lambda_2''}^*(\mathbf{q} - \mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \right\rangle + (1 \leftrightarrow 2). \end{aligned}$$

For the next step we notice that

$$\left\langle \sum_n \rho_{n,\lambda_2''}^*(\mathbf{q} - \mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2) \right\rangle = N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} S_{\lambda_2'' \lambda_2}(\mathbf{q}_2),$$

and with some properties of  $C(l_1 l_2 l; m_1 m_2 m)$  [34], we find that

$$\begin{aligned} &(-1)^{m_1} C(ll_1 l_2''; -mm_1 m_2'') a_{ll_1 l_2''}^\alpha \\ &= q_l^\alpha(\mathbf{q}) b_{l_1 l_2'' l}^\alpha(\mathbf{q} \cdot \mathbf{q}_1) C(l_1 l_2'' l; m_1 m_2'' m), \end{aligned}$$

with  $b_{l_1 l_2'' l}^\alpha(\mathbf{q} \cdot \mathbf{q}_1)$  from Eq. (56). Putting this together we arrive at

$$\begin{aligned} & \langle \mathcal{L}j_\lambda^\alpha(\mathbf{q})^* | \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \frac{kT}{I_\alpha} \sum_{\lambda_2''} b_{l_1 l_2''}^\alpha(\mathbf{q} \cdot \mathbf{q}_1) \\ & \quad \times C(l_1 l_2'' l; m_1 m_2'' m) S_{\lambda_2'' \lambda_2}(\mathbf{q}_2) + (1 \leftrightarrow 2) \end{aligned} \quad \mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q} \quad (\text{B6})$$

$$\begin{aligned} &= N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \frac{kT}{I_\alpha} \sum_{\lambda_1'' \lambda_2''} b_{l_1 l_2''}^\alpha(\mathbf{q} \cdot \mathbf{q}_1) C(l_1'' l_2'' l; m_1'' m_2'' m) \\ & \quad \times (\mathbf{S}^{-1}(\mathbf{q}_1))_{\lambda_1'' \lambda_2''} S_{\lambda_1'' \lambda_1}(\mathbf{q}_1) S_{\lambda_2'' \lambda_2}(\mathbf{q}_2) + (1 \leftrightarrow 2), \end{aligned} \quad (\text{B4})$$

where we introduced a factor  $\delta_{\lambda_1'' \lambda_1}$ . Replacing the inverse correlator by means of the Orstein-Zernike equation

$$(\mathbf{S}^{-1}(\mathbf{q}))_{\lambda \lambda'} = \delta_{\lambda \lambda'} - \frac{\rho_0}{4\pi} c_{\lambda \lambda'},$$

it follows that

$$\begin{aligned} & \langle \mathcal{L}j_\lambda^\alpha(\mathbf{q})^* | \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \frac{kT}{I_\alpha} \left\{ \sum_{\lambda_1'' \lambda_2''} [b_{l_1 l_2''}^\alpha(\mathbf{q} \cdot \mathbf{q}_1) C(l_1'' l_2'' l; m_1'' m_2'' m) \right. \\ & \quad + (1 \leftrightarrow 2)] S_{\lambda_1'' \lambda_1}(\mathbf{q}_1) S_{\lambda_2'' \lambda_2}(\mathbf{q}_2) \\ & \quad - \frac{\rho_0}{4\pi} \sum_{\lambda_1'' \lambda_2'' \lambda_3''} [b_{l_1 l_2''}^\alpha(\mathbf{q} \cdot \mathbf{q}_1) C(l_1'' l_2'' l; m_1'' m_2'' m) c_{\lambda_1'' \lambda_3''}(\mathbf{q}_1) \\ & \quad \left. \times S_{\lambda_1'' \lambda_1}(\mathbf{q}_1) S_{\lambda_2'' \lambda_2}(\mathbf{q}_2) + (1 \leftrightarrow 2)] \right\}. \end{aligned} \quad (\text{B5})$$

Substituting  $b_{l_1'' l_2''}^\alpha(\mathbf{q} \cdot \mathbf{q}_1)$  from Eq. (56) and making use of

$$\begin{aligned} & \sqrt{l_1(l_1+1)} C(l_1 l_2 l; 101) + \sqrt{l_2(l_2+1)} C(l_1 l_2 l; 011) \\ &= \sqrt{l(l+1)} C(l_1 l_2 l; 000), \end{aligned} \quad (\text{B7})$$

and

one can prove by use of the properties of  $C(l_1 l_2 l; m_1 m_2 m)$  [34] that

$$\begin{aligned} & [b_{l_1'' l_2''}^\alpha(\mathbf{q} \cdot \mathbf{q}_1) C(l_1'' l_2'' l; m_1'' m_2'' m) + (1 \leftrightarrow 2)] \\ &= q_i^\alpha(\mathbf{q}) b_{l_1'' l_2''} C(l_1'' l_2'' l; m_1'' m_2'' m), \end{aligned} \quad (\text{B8})$$

with

$$b_{l_1'' l_2''} = (-i)^{l_1'' + l_2''} \left( \frac{(2l_1'' + 1)(2l_2'' + 1)}{2l_1 + 1} \right)^{1/2} C(l_1'' l_2'' l; 000). \quad (\text{B9})$$

(ii) With  $P = P_\rho + P_j$  from Eqs. (38) and (39) we obtain, for the second term of Eq. (B1),

$$\begin{aligned} & \langle \mathcal{L}j_\lambda^\alpha(\mathbf{q})^* P | \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle = \frac{1}{N} \sum_{\lambda_1' \lambda_2'} (\mathbf{S}^{-1}(\mathbf{q}))_{\lambda_1' \lambda_2'} \langle \mathcal{L}j_\lambda^\alpha(\mathbf{q})^* | \delta\rho_{\lambda_1'}(\mathbf{q}) \rangle \langle \delta\rho_{\lambda_2'}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= \frac{1}{N} \sum_{\lambda_1' \lambda_2'} (\mathbf{S}^{-1}(\mathbf{q}))_{\lambda_1' \lambda_2'} \sum_{\alpha_1} \langle j_\lambda^\alpha(\mathbf{q})^* j_{\lambda_1'}^{\alpha_1}(\mathbf{q}) \rangle \langle \delta\rho_{\lambda_2'}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle \\ &= \frac{kT}{I_\alpha} \sum_{\lambda_2'} (\mathbf{S}^{-1}(\mathbf{q}))_{\lambda \lambda_2'} \langle \delta\rho_{\lambda_2'}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle, \end{aligned} \quad (\text{B10})$$

where we used again the hermiticity of  $\mathcal{L}$  and Eqs. (20) and (40). Unfortunately, the static three-point correlator in Eq. (B10) cannot be calculated exactly. In Appendix C it will be shown that it can be approximated as follows:

$$\langle \delta\rho_{\lambda_2'}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle \approx N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \sum_{\lambda_1'' \lambda_2'' \lambda_3''} b_{l_1'' l_2'' l_3''} C(l_1'' l_2'' l_3''; m_1'' m_2'' m_3'') S_{\lambda_2'' \lambda_3''}(\mathbf{q}) S_{\lambda_1'' \lambda_1}(\mathbf{q}_1) S_{\lambda_2'' \lambda_2}(\mathbf{q}_2).$$

With this, from Eq. (B10) we obtain

$$\langle \mathcal{L}j_\lambda^\alpha(\mathbf{q})^* P | \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \rangle \approx N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \frac{kT}{I_\alpha} \sum_{\lambda_1'' \lambda_2''} b_{l_1'' l_2''} C(l_1'' l_2'' l; m_1'' m_2'' m) S_{\lambda_1'' \lambda_1}(\mathbf{q}_1) S_{\lambda_2'' \lambda_2}(\mathbf{q}_2). \quad (\text{B11})$$

If we use Eq. (B8), the first term in the curly bracket of Eq. (B5) (including the prefactor) just cancels the second term (B11) of (B1). What remains for Eq. (B1) is the second term in the curly bracket which coincides with Eq. (54).

### APPENDIX C: APPROXIMATION OF $\langle \delta\rho_{\lambda_1}(\mathbf{q}_1)^* \delta\rho_{\lambda_2}(\mathbf{q}_2) \delta\rho_{\lambda_3}(\mathbf{q}_3) \rangle$

For *simple* liquids, Götze [1] used the factorization:

$$\langle \delta\rho(\mathbf{q}_1)^* \delta\rho(\mathbf{q}_2) \delta\rho(\mathbf{q}_3) \rangle \approx N \delta_{\mathbf{q}_1, \mathbf{q}_2 + \mathbf{q}_3} S(\mathbf{q}_1) S(\mathbf{q}_2) S(\mathbf{q}_3) \quad (\text{C1})$$

in  $\mathbf{q}$  space. We require that the approximation of the three-point correlator for *molecular* liquids should obey the correct transformation properties and that it reduces to Eq. (C1) for  $\lambda_1 = \lambda_2 = \lambda_3 = (0,0)$ . We choose the approximation

$$\begin{aligned} \langle \delta\rho_{\lambda_1}(\mathbf{q}_1)^* \delta\rho_{\lambda_2}(\mathbf{q}_2) \delta\rho_{\lambda_3}(\mathbf{q}_3) \rangle &= (4\pi)^{3/2} i^{l_2 + l_3 - l_1} \int \prod_{j=1}^3 d^2\Omega_j \langle \delta\rho(\mathbf{q}_1, \Omega_1)^* \delta\rho(\mathbf{q}_2, \Omega_2) \\ &\quad \times \delta\rho(\mathbf{q}_3, \Omega_3) \rangle Y_{\lambda_1}^*(\Omega_1) Y_{\lambda_2}(\Omega_2) Y_{\lambda_3}(\Omega_3) \\ &\approx i^{l_2 + l_3 - l_1} (4\pi)^{3/2} (4\pi/N)^2 \int \prod_j (d^2\Omega_j d^2\Omega'_j) \int d^2\Omega \prod_j \delta(\Omega, \Omega'_j) Y_{\lambda_1}^*(\Omega_1) Y_{\lambda_2}(\Omega_2) Y_{\lambda_3}(\Omega_3) \\ &\quad \times \langle \delta\rho(\mathbf{q}_1, \Omega_1)^* \delta\rho(\mathbf{q}_1, \Omega'_1) \delta\rho(\mathbf{q}_2, \Omega_2) \delta\rho(\mathbf{q}_2, \Omega'_2)^* \delta\rho(\mathbf{q}_3, \Omega_3) \delta\rho(\mathbf{q}_3, \Omega'_3)^* \rangle. \end{aligned}$$

Factorization of the six-point correlator

$$\begin{aligned} \langle \delta\rho(\mathbf{q}_1, \Omega_1)^* \delta\rho(\mathbf{q}_1, \Omega'_1) \delta\rho(\mathbf{q}_2, \Omega_2) \delta\rho(\mathbf{q}_2, \Omega'_2)^* \delta\rho(\mathbf{q}_3, \Omega_3) \delta\rho(\mathbf{q}_3, \Omega'_3)^* \rangle \\ \approx N^3 S(\mathbf{q}_1, \Omega_1, \Omega'_1) S(\mathbf{q}_2, \Omega_2, \Omega'_2)^* S(\mathbf{q}_3, \Omega_3, \Omega'_3)^* \delta_{\mathbf{q}_1, \mathbf{q}_2 + \mathbf{q}_3}, \end{aligned} \quad (\text{C2})$$

where

$$S(\mathbf{q}, \Omega, \Omega') = \frac{1}{N} \langle \delta\rho(\mathbf{q}, \Omega)^* \delta\rho(\mathbf{q}, \Omega') \rangle, \quad (\text{C3})$$

and using that

$$\int d^2\Omega \int d^2\Omega' S(\mathbf{q}, \Omega, \Omega') Y_{\lambda}^*(\Omega) Y_{\lambda'}(\Omega') = \frac{1}{4\pi} i^l (-i)^{l'} S_{\lambda\lambda'}(\mathbf{q}), \quad (\text{C4})$$

$$\int d^2\Omega \prod_j \delta(\Omega, \Omega'_j) = (4\pi)^{-1/2} \sum_{\lambda_1'' \lambda_2'' \lambda_3''} b_{l_1'' l_2'' l_3''} C(l_1'' l_2'' l_3''; m_1'' m_2'' m_3'') Y_{\lambda_1''}(\Omega'_1) Y_{\lambda_2''}^*(\Omega'_2) Y_{\lambda_3''}^*(\Omega'_3) \quad (\text{C5})$$

leads to

$$\langle \delta\rho_{\lambda_1}(\mathbf{q}_1)^* \delta\rho_{\lambda_2}(\mathbf{q}_2) \delta\rho_{\lambda_3}(\mathbf{q}_3) \rangle \approx N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \sum_{\lambda_1'' \lambda_2'' \lambda_3''} b_{l_1'' l_2'' l_3''} C(l_1'' l_2'' l_3''; m_1'' m_2'' m_3'') S_{\lambda_1 \lambda_1''}(\mathbf{q}_1) S_{\lambda_2 \lambda_2''}(\mathbf{q}_2) S_{\lambda_3 \lambda_3''}(\mathbf{q}_3), \quad (\text{C6})$$

which is the result we used in Appendix B. It is easy to prove that Eq. (C6) reduces to Eq. (C1) if  $\lambda_i \equiv (0,0)$  and  $\lambda_i'' \equiv (0,0)$ , and that it possesses the correct symmetry under  $R \in O(3)$ .

### APPENDIX D: VERTICES FOR $\mathbf{q} \rightarrow \mathbf{0}$

Due to  $\mathbf{q} = \mathbf{q}_1 + \mathbf{q}_2$ , it follows that  $\mathbf{q}_2 \rightarrow -\mathbf{q}_1$  for  $\mathbf{q} \rightarrow \mathbf{0}$ . Therefore, we may write  $\mathbf{q}_2$  as

$$\mathbf{q}_2 = \mathbf{q}_1 (-1 + \mathbf{q} \cdot \boldsymbol{\varepsilon}), \quad |\boldsymbol{\varepsilon}| = O(1). \quad (\text{D1})$$

Then we obtain with

$$c_{\lambda\lambda'}(\mathbf{q}_2) = c_{\lambda\lambda'}(-\mathbf{q}_1) + O(\mathbf{q}) = (-1)^{l+l'+m+m'} c_{\bar{\lambda}'\bar{\lambda}}(\mathbf{q}_1) + O(\mathbf{q}), \quad (\text{D2})$$

where Eqs. (24) and (25) [which also hold for  $c_{\lambda\lambda'}(q)$ ] and  $\bar{\lambda} = (l, -m)$  were used, that



$$\begin{aligned}
\sum_{\lambda''} v^\alpha(\mathbf{q}, \lambda | \mathbf{q}_1 \lambda_1; \mathbf{q}_2 \lambda_2; \lambda'') &= \sum_{\lambda''} [b_{l''l_2l}^\alpha(\mathbf{q}, \mathbf{q}_1) C(l''l_2l; m''m_2m) c_{\lambda''\lambda_1}(\mathbf{q}_1) \\
&\quad + (-1)^{l_2+l''+m_2+m''} b_{l''l_1l}^\alpha(-\mathbf{q}, \mathbf{q}_1) C(l''l_1l; m''m_1m) c_{\lambda_2\lambda''}(\mathbf{q}_1)] + O(\mathbf{q}) \\
&= \sum_{\lambda''(\neq\lambda_2)} b_{l''l_2l}^\alpha(\mathbf{q}, \mathbf{q}_1) C(l''l_2l; m''m_2m) c_{\lambda''\lambda_1}(\mathbf{q}_1) + \sum_{\lambda''(\neq\lambda_1)} (-1)^{l_2+l''+m_2+m''} b_{l''l_1l}^\alpha(-\mathbf{q}, \mathbf{q}_1) \\
&\quad \times C(l''l_1l; m''m_1m) c_{\lambda_2\lambda''}(\mathbf{q}_1) \\
&\quad + [b_{l_2l_2l}^\alpha(\mathbf{q}, \mathbf{q}_1) C(l_2l_2l; -m_2m_2m) + (-1)^{l_1+l_2+m_1+m_2} b_{l_1l_1l}^\alpha(-\mathbf{q}, \mathbf{q}_1) \\
&\quad \times C(l_1l_1l; -m_1m_1m)] c_{\lambda_2\lambda_1}(\mathbf{q}_1) + O(\mathbf{q}). \tag{D3}
\end{aligned}$$

For  $l \neq 0$  the restricted sum in Eq. (D3) is generically non-zero. Therefore, it is for  $l \neq 0$ ,

$$\sum_{\lambda''} v^\alpha(\mathbf{q}, \lambda | \mathbf{q}_1 \lambda_1; \mathbf{q}_2 \lambda_2; \lambda'') = O(1). \tag{D4}$$

For  $\lambda = (0,0)$  the Clebsch-Gordon coefficients  $C(l_1l_20; m_1m_20)$  are nonzero for  $l_1=l_2$  and  $m_1+m_2=0$  only. Therefore, both restricted sums in Eq. (D3) do vanish, and it remains

$$\begin{aligned}
\sum_{\lambda''} v^\alpha(\mathbf{q}, \lambda | \mathbf{q}_1 \lambda_1; \mathbf{q}_2 \lambda_2; \lambda'') &= [b_{l_2l_20}^\alpha(\mathbf{q}, \mathbf{q}_1) C(l_2l_20; -m_2m_20) \\
&\quad + (-1)^{l_1+l_2+m_1+m_2} b_{l_1l_10}^\alpha(-\mathbf{q}, \mathbf{q}_1) \\
&\quad \times C(l_1l_10; -m_1m_10)] c_{\lambda_2\lambda_1}(\mathbf{q}_1) + O(\mathbf{q}) \\
&= \begin{cases} O(q), & \alpha = T \\ O(l), & \alpha = R, \end{cases} \tag{D5}
\end{aligned}$$

where Eqs. (56) and (B6) has been used.

#### APPENDIX E: RESULT FOR $c_l^m(\mathbf{q})$

The direct correlation function  $c_{lm;l'm'}(\mathbf{q})$  becomes diagonal in the  $q$  frame and in the MSA.

$$c_{lm;l'm'}(\mathbf{q}, \mathbf{t}) \cong c_l^m(\mathbf{q}) \delta_{ll'} \delta_{mm'}. \tag{E1}$$

To calculate  $c_{lm;l'm'}(\mathbf{q}, t)$  from Eq. (73) it is important to note that we keep  $\mathbf{q} \neq \mathbf{0}$  and perform the limit volume  $V \rightarrow \infty$  first, and afterwards the limit  $\mathbf{q} \rightarrow \mathbf{0}$  can be taken. One has to be cautious with these two limits due to the long-range character of the dipolar interactions, which leads to a  $r^{-3}$  decay for  $c_D(r)$  [cf. Eq. (68)]. As a result we obtain

$$\begin{aligned}
c_0^0(y) &= 16\pi^2 d^3 y^{-6} \{ [24c_3 - 2c_1] y^2 \\
&\quad + [-24c_3 y + (c_0 + 2c_1 + 4c_3) y^3] \sin y \\
&\quad + [-24c_3 + (2c_1 + 12c_3) y^2 \\
&\quad - (c_0 + c_1 + c_3) y^4] \cos y \}, \tag{E2}
\end{aligned}$$

$$\begin{aligned}
c_1^0(y) &= 16\pi^2 d^3 y^{-6} \left\{ [8(c_\Delta^{(3)} + 4c_D^{(3)}) - \frac{2}{3}(c_\Delta^{(1)} + 8c_D^{(1)}) y^2] \right. \\
&\quad + \left[ -8(c_\Delta^{(3)} + 4c_D^{(3)}) y + \frac{1}{3} \left( c_\Delta^{(0)} + 2c_\Delta^{(1)} + 4c_\Delta^{(3)} \right. \right. \\
&\quad \left. \left. + 10c_D^{(1)} + 14c_D^{(3)} - 2 \frac{\beta\mu^2}{d^3} \right) y^3 \right] \sin y \\
&\quad + \left[ -8(c_\Delta^{(3)} + 4c_D^{(3)}) + \left( \frac{2}{3}c_\Delta^{(1)} + 4c_\Delta^{(3)} + \frac{16}{3}c_D^{(1)} \right. \right. \\
&\quad \left. \left. + 16c_D^{(3)} \right) y^2 - \frac{1}{3} \left( c_\Delta^{(0)} + c_\Delta^{(1)} + c_\Delta^{(3)} + 2c_D^{(1)} \right. \right. \\
&\quad \left. \left. + 2c_D^{(3)} - 2 \frac{\beta\mu^2}{d^3} \right) y^4 \right] \cos y \left. \right\} \tag{E3}
\end{aligned}$$

and

$$\begin{aligned}
c_1^1(y) &= 16\pi^2 d^3 y^{-6} \left\{ [8(c_\Delta^{(3)} - 2c_D^{(3)}) - \frac{2}{3}(c_\Delta^{(1)} - 4c_D^{(1)}) y^2] \right. \\
&\quad + \left[ -8(c_\Delta^{(3)} - 2c_D^{(3)}) y + \frac{1}{3} \left( c_\Delta^{(0)} + 2c_\Delta^{(1)} + 4c_\Delta^{(3)} \right. \right. \\
&\quad \left. \left. - 5c_D^{(1)} - 7c_D^{(3)} + \frac{\beta\mu^2}{d^3} \right) y^3 \right] \sin y + \left[ -8(c_\Delta^{(3)} - 2c_D^{(1)}) \right. \\
&\quad \left. + \left( \frac{2}{3}c_\Delta^{(1)} + 4c_\Delta^{(3)} - \frac{8}{3}c_D^{(1)} - 8c_D^{(3)} \right) y^2 - \frac{1}{3} \left( c_\Delta^{(0)} + c_\Delta^{(1)} \right. \right. \\
&\quad \left. \left. + c_\Delta^{(3)} - c_D^{(1)} - c_D^{(3)} + \frac{\beta\mu^2}{d^3} \right) \right] \cos y \left. \right\}, \tag{E4}
\end{aligned}$$

where  $y = qd$  is the dimensionless wave number and

$$\begin{aligned}
c_\Delta^{(\nu)} &= 2\kappa [c_\nu(2\kappa\varphi) - c_\nu(-\kappa\varphi)], \quad \nu = 0, 1, 3 \\
c_D^{(1)} &= \frac{1}{4}\kappa [2c_1(2\kappa\varphi) + c_1(-\kappa\varphi)], \tag{E5} \\
c_D^{(3)} &= \frac{1}{2}\kappa [2c_3(2\kappa\varphi) + c_3(-\kappa\varphi)].
\end{aligned}$$

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