

A Mode Coupling Approach to the Ideal Glass Transition of Molecular Liquids: Linear Molecules

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Abstract:

The mode coupling theory for the ideal liquid glass transition which was worked out for *simple* liquids mainly by Götze, Sjögren and their coworkers, 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 $S_{\ell m, \ell' m'}(\mathbf{q}, t)$ of the tensorial one-particle density $\rho_{\ell m}(\mathbf{q}, t)$, which contains the orientational degrees of freedom for $\ell > 0$. Application of the mode coupling approximation to the memory kernel results into a *closed* set of equations for $S_{\ell m, \ell' m'}(\mathbf{q}, t)$, which requires the static correlators $S_{\ell m, \ell' m'}(\mathbf{q})$ as the only input quantities.

The corresponding MCT-equations for the non-ergodicity parameters $f_{\ell}^m(\mathbf{q}) \equiv f_{\ell m, \ell m}(\mathbf{q} \mathbf{e}_3)$ are solved for a system of dipolar hard spheres by restricting the values for ℓ to 0 and 1. Depending on the packing fraction ϕ and on the temperature T , three different phases exist: a liquid phase, where translational (TDOF) ($\ell = 0$) *and* orientational (ODOF) ($\ell = 1$) degrees of freedom are ergodic, a phase where the TDOF are frozen into a (non-ergodic) glassy state whereas the ODOF remain ergodic, and finally a glassy phase where both, TDOF and ODOF, are non-ergodic. From the non-ergodicity parameters $f_0^0(\mathbf{q})$ and $f_1^1(\mathbf{q})$ for $\mathbf{q} = 0$, we may conclude that the corresponding relaxation strength of the α -peak of the compressibility can be much smaller than the corresponding strength of the dielectric function.

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1. 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 coworkers. 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 [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:

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

where Ω_q is the microscopic frequency:

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

Separating the fast and slow part, 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 ν_q and

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

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 v_q) the dynamics is uniquely determined by the static correlator S_q . We also mention that the r.h.s. of (2d) is the first term in a polynomial expansion of $M_q(t)$ into products

$$\phi_{\mathbf{q}_1}(t) \dots \phi_{\mathbf{q}_m}(t) \text{ with } m \geq 2.$$

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 ρ_c) at which a *dynamical transition* takes place from an ergodic to a non-ergodic phase. This transition can be interpreted as a glass transition. As an order parameter one chooses the *non-ergodicity 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 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_σ and τ . For the *α -relaxation regime*, where t is of order τ , there exists a master function $\bar{\phi}_q(\bar{t})$ such that

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

In the so-called *β -relaxation regime* (not to be confused with the β -process) one finds the power law behaviour:

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

$$(5b)$$

$f_q^c \equiv f_q(T_c)$ is the non-ergodicity parameter at T_c and $t_0 \approx \Omega_q^{-1}$ is a microscopic time scale.

The temperature dependence of t_σ and τ is given by

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

and

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

with $\gamma = \frac{1}{2a} + \frac{1}{2b}$. 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 λ ($0 < \lambda < 1$):

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

where Γ is the gamma function. λ 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 identify hopping processes to be responsible for restoring ergodicity. Another interesting MCT-approach was recently given by Schmitz et al. [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 behaviour of the α -peak width for $q \rightarrow 0$, which, however, has been recently clarified by Latz and Schmitz [8]. Despite the necessity to use this *extended* MCT, several experimental (e.g. [2]-[3]) and numerical investigations (e.g. [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) which are probed by dielectric spectroscopy, couples to the translational degrees of freedom (TDOF), i.e. to the density fluctuations, MCT predicts for e.g. the dipole correlator a power law behaviour as described by (5) with the *same* exponents. This implies that the imaginary part $\kappa_q''(\omega)$ and $\epsilon''(\omega)$ of the compressibility and dielectric function, respectively, exhibit for $T > T_c$ a minimum at the *same* frequency ω_{\min} . Whereas $\kappa_q''(\omega)$ obtained from light and neutron scattering experiments shows an MCT-minimum for Glycerol [13], Salol [14], CKN [15], [16] and OTP [17], no minimum was found in the dielectric experiments for Glycerol [18] and Salol [18]. For OTP $\epsilon''(\omega)$ possesses a β -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 his coworkers have found very recently a minimum in $\epsilon''(\omega)$ 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* for the existence of a minimum in $\epsilon''(\omega)$ has been found, without specifying its position. The status for 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 and ODOF. Apart from the orientational glass phases of mixed crystals [23] for which MCT was worked out by Michel and coworkers [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 has been 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 has already been 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 details the reader is referred to

the recent review by Bagchi and Chandra [28]. There is strong numerical evidence from MD-simulations that even the ODOF do exhibit non-exponential 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. The next section presents the various correlation functions and its symmetry properties. The MCT-approach is discussed in its general form for linear molecules in section 3 and applied to a system of dipolar hard spheres in section 4. The last section 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.

2. 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 . The TDOF 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 $\{\ell_n\} = (\ell_1, \dots, \ell_N)$ as orientational coordinates, where $\Omega_n = (\phi_n, \theta_n)$ are the Euler angles of the n -th molecule and $\ell_n = \mathbf{I}(\Omega_n) \omega_n$ is the corresponding angular momentum. The linear and angular velocities are, respectively, \mathbf{v}_n and ω_n . The third Euler angle χ_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:

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

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

$$\ell_n' = \mathbf{R}(\Omega_n) \ell_n \quad , \quad \omega_n' = \mathbf{R}(\Omega_n) \omega_n \quad (9)$$

and

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

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

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

$\delta(\Omega, \Omega')$ 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:

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

with the coefficients:

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

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

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

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

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

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

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

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

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

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

with:

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

and the corresponding current density correlator:

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

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

$$i\ell \rho_{\ell m}(\mathbf{q}, t) \equiv \dot{\rho}_{\ell m}(\mathbf{q}, t) = i \sum_{\alpha} \left(\hat{\mathbf{q}}^{\alpha} \mathbf{j}_{\ell m}^{\alpha} \right) (\mathbf{q}, t) \quad (20)$$

where ℓ is the corresponding *Liouvillean*, and as a short hand notation we use the operator

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

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

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

where

$$\begin{aligned} L_{\ell, mm'}^1 \pm i L_{\ell, mm'}^2 &\equiv L_{\ell, mm'}^{\pm} = [\ell(\ell+1) - m(m \pm 1)]^{1/2} \delta_{m', m \pm 1} \\ L_{\ell, mm'}^3 &= m \delta_{m'm} \quad . \end{aligned} \quad (23)$$

Now we discuss the various properties of $S_{\ell m, \ell' m'}(\mathbf{q}, t)$. Similar properties hold for $J_{\ell m, \ell' m'}^{\alpha k; \alpha' k'}(\mathbf{q}, t)$. This discussion is like that by Blum et al. [35] who use 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 the definition (15):

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

i.e. the matrix $\mathbf{S}(\mathbf{q}, t) = (S_{\ell m, \ell' m'}(\mathbf{q}, t))$ is *hermitean*. On the other hand we may use (16) and the behaviour of $Y_{\ell m}(\Omega)$ under complex conjugation. This yields:

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

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

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

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

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

The angular brackets in (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:

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

and

$$J_{\ell m; \ell' m'}^{\alpha k; \alpha' k'}(\mathbf{R}\mathbf{q}, t) = \sum_{k_1, k_1'} \sum_{m_1, m_1'} R_{k k_1} R_{k' k_1'} D_{m_1 m}^{\ell*}(\mathbf{R}) D_{m_1 m'}^{\ell'}(\mathbf{R}) J_{\ell m_1; \ell' m_1'}^{\alpha k_1; \alpha' k_1'}(\mathbf{q}, t) \quad (29)$$

What remains is the behaviour under *inversion* P . Since $Y_{\ell m}(P\Omega) = (-1)^\ell Y_{\ell m}(\Omega)$, it follows from (16) and (19):

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

and

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

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 $D_{m' m}^\ell(\mathbf{R}) = e^{-im\phi} \delta_{mm'}$, [34]. In that case we obtain from (28):

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

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

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

For the current density correlator this is true for $J_{\ell m; \ell' m'}^{\alpha 3; \alpha' 3}(\mathbf{q}_0, t)$, 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 $D_{m' m}^{\ell}(R_2) = (-1)^{\ell+m} \delta_{m, -m'}$ [34], we get from (28):

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

which together with (25) and (32) yields

$$\left(S_{\ell \ell'}^m(\mathbf{q}, t) \right)^* = S_{\ell \ell'}^m(\mathbf{q}, t) \quad , \quad (34)$$

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

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

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

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

3. Mode coupling approach

The correlators $S_{\ell m; \ell' m'}(\mathbf{q}, t)$ are of experimental and theoretical interest. For $\ell = \ell' = 0$ 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 $\ell = \ell' = 1$ contains

information which can be obtained from dielectric measurements and $\ell = \ell' = 2$ 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 $S_{\ell m, \ell' m'}(\mathbf{q}, t)$. The following short hand notation is convenient: $(\mathbf{q}, \ell, m) = 0$, $(\mathbf{q}, \ell', m') = 0'$, $(\mathbf{q}_i, \ell_i, m_i) = i$ and $(\ell, m) = \lambda$. The use of this formalism requires the specification of the slow variables. Because we study glassy dynamics, it is obvious that $\delta\rho_{\ell m}(\mathbf{q}) \equiv \delta\rho(0)$ 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:

$$j^{\alpha} (0) \equiv j_{\ell m}^{\alpha}(\mathbf{q}) = \frac{1}{q_{\ell}^{\alpha}(\mathbf{q})} \left(\hat{\mathbf{q}}^{\alpha} \mathbf{j}^{\alpha} \right)_{\ell m}(\mathbf{q}) \quad (36)$$

for $\alpha = T$ and R, where

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

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. [38]) which generates a *coupling* between the *longitudinal* and *transversal* components of the current density, is under investigation. The energy density $\varepsilon_{\ell m}(\mathbf{q})$ will be omitted as a slow variable, as it was done for the 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

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

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

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

where the latter equality is proven in Appendix A. I_α is the unified notation:

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

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

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

of the density correlator:

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

with

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

The next projection step yields for the momentum density correlator:

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

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

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

Here, $Q = 1 - P = 1 - (P_p + P_j)$ projects perpendicular 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 $\left| F_{\ell m}^{\alpha}(\mathbf{q}) \right\rangle = Q \left| \mathcal{L} j_{\ell m}^{\alpha}(\mathbf{q}) \right\rangle$. Since the interaction between the molecules is assumed to be *pairwise*, we project $\left| F_{\ell m}^{\alpha}(\mathbf{q}) \right\rangle$ onto a product of *two* density modes. This is done in a close relationship to the case of a simple liquid which is clearly discussed by Götze [1]. Following ref. [1] we define the projector on pairs of modes:

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

where the normalization matrix g must fulfil:

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

with the symmetrized Kronecker-delta:

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

and the obvious meaning $\delta(1,1') \equiv \delta_{\mathbf{q}_1 \mathbf{q}_1} \cdot \delta_{\ell_1 \ell_1} \cdot \delta_{m_1 m_1}$. Using the following approximations:

$$(i) \quad \left| F^{\alpha}(0) \right\rangle \approx \rho \left| F^{\alpha}(0) \right\rangle \quad (50)$$

$$(ii) \quad \langle \delta\rho(1) * \delta\rho(2) * |Qe^{-iQ\ell Q^t} Q| \delta\rho(1')\delta\rho(2') \rangle \quad (51)$$

$$\approx N^2 [S(1,1';t)S(2,2';t) + (1' \leftrightarrow 2')]$$

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

we get

$$M^{\alpha\alpha'}(0,0';t) \approx \frac{1}{2N^3} \sum_{121'2'} \sum_{343'4'} \mathbf{S}^{-1}(1,1')\mathbf{S}^{-1}(2,2')\mathbf{S}^{-1}(3,3')\mathbf{S}^{-1}(4,4').$$

$$\left\langle \mathcal{L}^{\alpha} j^{\alpha'}(0) * Q \left| \delta\rho(1)\delta\rho(2) \right\rangle \left\langle \delta\rho * (3')\delta\rho * (4') \right| Q \mathcal{L}^{\alpha'} j^{\alpha'}(0) \right\rangle.$$

$$S(1',3;t)S(2',4;t) \quad . \quad (53)$$

In Appendices B and C it is shown that

$$\left\langle \mathcal{L}^{\alpha} j^{\alpha}(\mathbf{q}) * Q \left| \delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle \approx -\frac{\rho_0}{4\pi} N \delta_{\mathbf{q}_1+\mathbf{q}_2,\mathbf{q}} \frac{kT}{I_{\alpha}}.$$

$$\sum_{\lambda_1\lambda_2\lambda} \left[u^{\alpha}(\mathbf{q}\lambda|\mathbf{q}_1\lambda_1;\mathbf{q}_2\lambda_2) c_{\lambda_1\lambda}(\mathbf{q}_1) S_{\lambda\lambda_1}(\mathbf{q}_1) S_{\lambda_2\lambda_2}(\mathbf{q}_1) + (1 \leftrightarrow 2) \right]$$

$$(54)$$

with

$$u^{\alpha}(\mathbf{q}\lambda|\mathbf{q}_1\lambda_1;\mathbf{q}_2\lambda_2) = b_{\ell_1\ell_2\ell}^{\alpha}(\mathbf{q}\mathbf{q}_1) C(\ell_1\ell_2\ell; m_1 m_2 m) \quad (55)$$

and

$$b_{\ell_1\ell_2\ell}^{\alpha}(\mathbf{q}\mathbf{q}_1) = i^{\ell_1+\ell_2-\ell} \left(\frac{(2\ell_1+1)(2\ell_2+1)}{2\ell+1} \right)^{1/2} \frac{1}{2} \left[1 + (-1)^{\ell_1+\ell_2+\ell} \right].$$

(56)

$$\left\{ \begin{array}{l} \frac{1}{q}(\mathbf{q}\mathbf{q}_1)C(\ell_1\ell_2\ell;000) \quad , \quad \alpha = T \\ \sqrt{\ell_1(\ell_1+1)}C(\ell_1\ell_2\ell;101), \quad \alpha = R \end{array} \right.$$

where $C(\ell_1\ell_2\ell; m_1m_2m)$ are the Clebsch-Gordon 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:

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

and $\rho_0 = N/V$ is the average number density. The reader should note that the prefactor $(kT/I_\alpha) \cdot (kT/I_\alpha)$ which appears for $M^{\alpha\alpha'}(0,0;t)$ after substitution of (54) into (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 (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 $\mathbf{J}^{-1} \mathbf{M}(\mathbf{q},t) \mathbf{J}^{-1}$

$$\left[\left(\mathbf{J}^{-1} \mathbf{M}(\mathbf{q},t) \mathbf{J}^{-1} \right)_{\lambda\lambda'}^{\alpha\alpha'} \right]_{\text{slow}} \approx m_{\lambda\lambda'}^{\alpha\alpha'}(\mathbf{q},t) =$$

$$= \frac{1}{2N} \sum_{\mathbf{q}_1\mathbf{q}_2} \sum_{\substack{\lambda_1\lambda_1' \\ \lambda_2\lambda_2'}} V^{\alpha\alpha'} \left(\mathbf{q}\lambda\lambda' \left| \mathbf{q}_1\lambda_1\lambda_1'; \mathbf{q}_2\lambda_2\lambda_2' \right. \right). \quad (58)$$

$$\cdot S_{\lambda_1\lambda_1'}(\mathbf{q}_1,t) S_{\lambda_1\lambda_1'}(\mathbf{q}_2,t)$$

with the vertices

$$V^{\alpha\alpha'} \left(\mathbf{q}\lambda\lambda' \left| \mathbf{q}_1\lambda_1\lambda_1'; \mathbf{q}_2\lambda_2\lambda_2' \right. \right) =$$

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

where

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

Neglecting the regular part $\left[\left(\mathbf{J}^{-1} \mathbf{M}(\mathbf{q}, t) \mathbf{J}^{-1} \right)_{\lambda\lambda'}^{\alpha\alpha'} \right]_{\text{reg}}$, the eqs. (43)-(45), (58)-(60), together

with (40), (55) and (56) are a closed set equations for the density correlator $S_{\ell m, \ell' m'}(\mathbf{q}, t)$ with the static correlators $S_{\ell m, \ell' m'}(\mathbf{q})$ as input quantities.

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

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

which implies

$$v^{\text{TT}}(\mathbf{q}, 00, 00 | \mathbf{q}_1\lambda_1\lambda_1'; \mathbf{q}_2\lambda_2\lambda_2') = 0(\mathbf{q}^2)$$

$$v^{\text{TR}}(\mathbf{q}, 00, \ell' m' | \mathbf{q}_1\lambda_1\lambda_1'; \mathbf{q}_2\lambda_2\lambda_2') = 0(\mathbf{q}) \quad (62)$$

$$v^{\text{RT}}(\mathbf{q}, \ell m, 00 | \mathbf{q}_1\lambda_1\lambda_1'; \mathbf{q}_2\lambda_2\lambda_2') = 0(\mathbf{q})$$

all others $= 0(1)$.

This behaviour relates to the fact that $\mathbf{j}_{\ell m}^T(\mathbf{q})$, in contrast to $\mathbf{j}_{\ell m}^R(\mathbf{q})$, is a conserved quantity for $\mathbf{q} = 0$ 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 $t_g(T)$ on which the \mathbf{q} - and t -dependence of the density correlator factorizes and that its t -dependence is given by a correlator $G(t)$ which depends on the exponent parameter λ , only. λ follows from the static correlator $S(\mathbf{q})$ for $T = T_c$, i.e. λ 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 the next section, the vertices become real and positive. Despite the different structure of the MCT-equations for $\ell > 0$ (cf. eq. (78)), one can still prove that the reduction theorem is valid and that $G(t)$ fulfils the same "universal" equation derived by Götze [39] for simple liquids. The only difference is that the microscopic calculation of λ also involves the static density correlators $S_{\ell m, \ell m}(\mathbf{q})$ for $\ell \geq 0$.

4. MCT for dipolar hard spheres

In this section we will apply the MCT-equations which were derived in section 3 to a system of dipolar hard spheres (DHS). This system consists of hard spheres with diameter d and a dipolar moment μ . Besides the hard sphere interaction $V_{hs}(\{\mathbf{x}_n\})$, 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 $\mu = |\mu|$ and $\mathbf{e}_n = \mu/|\mu|$, the unit vector pointing in the direction of Ω_n . We choose this system because of 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 MCT [40],[41]. Therefore, our MCT-approach which includes ODOF may be a good approximation for DHS, 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 $\mu_n \rightarrow -\mu_n$ for all n , yields an additional restriction for $S_{\ell m, \ell' m'}(\mathbf{q}, t)$ which is:

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

Let us now discuss $c(\mathbf{x},\Omega,\Omega')$. Wertheim [42] has shown that within the mean spherical approximation (MSA) (cf. also [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 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

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

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

where $r = |\mathbf{x}|$, $\mathbf{e}_x = \mathbf{x}/r$ and \mathbf{e}, \mathbf{e}' are unit vectors pointing in the direction of Ω, Ω' , 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 $\left(\beta = \frac{1}{kT}\right)$ 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 μ^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 Percus-Yevick approximation is given by [34]

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

with

$$\begin{aligned} c_0(\varphi) &= -(1 + 2\varphi)^2/(1 - \varphi)^4 \\ c_1(\varphi) &= 6\varphi(1 + \varphi/2)^2/(1 - \varphi)^4 \\ c_3(\varphi) &= \varphi c_0(\varphi)/2 \end{aligned} \quad (72)$$

The calculation of

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

is straightforward. As shown in section 2 it is convenient to use the \mathbf{q} -frame. The explicit expressions for $c_{\ell \ell'}^m(\mathbf{q})$ are presented in Appendix E. From this appendix it follows:

$$c_{\ell\ell'}^m(\mathbf{q}) = c_\ell^m(\mathbf{q})\delta_{\ell\ell'}, \quad (74)$$

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

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

for $\ell = 0, 1$ and $\ell' = 0, 1$. Consequently, only three independent correlators $S_0^0(\mathbf{q}, t)$, $S_1^0(\mathbf{q}, t)$ and $S_1^1(\mathbf{q}, t)$ exist. Because the inclusion of ODOF has made the MCT-equations much 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 non-ergodicity parameter

$$f_\ell^m(\mathbf{q}) = \lim_{t \rightarrow \infty} S_\ell^m(\mathbf{q}, t) / S_\ell^m(\mathbf{q}) \quad (76)$$

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

$$\frac{f_0^0(\mathbf{q})}{1 - f_0^0(\mathbf{q})} = \left(\mathcal{F}^T \right)_0^0 \left(\mathbf{q}; \left\{ f_\ell^m \right\} \right) \quad (77)$$

and

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

for $m = 0, 1$. Here we performed one more *approximation* which is the diagonalization of the memory kernel with respect to α and α' . Due to this, the vertices become *real* and *non-*

negative. The reader should not confuse the superscript T with temperature. The functionals

$\left(\mathcal{F}^\alpha\right)_\ell^m\left(\mathbf{q};\left\{f_\ell^m\right\}\right)$ follow from $m_{\ell m;\ell' m'}^{\alpha\alpha}(\mathbf{q},t)$ after transformation to the q -frame and are of

the form:

$$\left(\mathcal{F}^\alpha\right)_\ell^m\left(\mathbf{q};\left\{f_\ell^m\right\}\right)=\int_0^\infty d\mathbf{q}_1 \int_{|\mathbf{q}-\mathbf{q}_1|}^{\mathbf{q}+\mathbf{q}_1} d\mathbf{q}_2 \left(\mathcal{H}^\alpha\right)_\ell^m\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2;\left\{f_\ell^m\right\}\right)$$

with

$$\begin{aligned} \left(\mathcal{H}^T\right)_0^0\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2;\left\{f_\ell^m\right\}\right) &= \left(\mathbf{V}_{00,00}^T\right)_0^0\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2\right) f_0^0\left(\mathbf{q}_1\right) f_0^0\left(\mathbf{q}_2\right) + \\ &+ \left(\mathbf{V}_{11,10}^T\right)_0^0\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2\right) \left[f_1^1\left(\mathbf{q}_1\right) f_1^0\left(\mathbf{q}_2\right) + f_1^1\left(\mathbf{q}_2\right) f_1^0\left(\mathbf{q}_1\right) \right] + \\ &+ \left(\mathbf{V}_{10,10}^T\right)_0^0\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2\right) f_1^0\left(\mathbf{q}_1\right) f_1^0\left(\mathbf{q}_2\right) + \\ &+ \left(\mathbf{V}_{11,11}^T\right)_0^0\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2\right) f_1^1\left(\mathbf{q}_1\right) f_1^1\left(\mathbf{q}_2\right) \end{aligned} \quad (79)$$

and

$$\begin{aligned} \left(\mathcal{H}^\alpha\right)_1^m\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2;\left\{f_\ell^m\right\}\right) &= \left(\mathbf{V}_{00,10}^\alpha\right)_1^m\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2\right) \left[f_0^0\left(\mathbf{q}_1\right) f_1^0\left(\mathbf{q}_2\right) + f_0^0\left(\mathbf{q}_2\right) f_1^0\left(\mathbf{q}_1\right) \right] + \\ &+ \left(\mathbf{V}_{00,11}^\alpha\right)_1^m\left(\mathbf{q},\mathbf{q}_1,\mathbf{q}_2\right) \left[f_0^0\left(\mathbf{q}_1\right) f_1^1\left(\mathbf{q}_2\right) + f_0^0\left(\mathbf{q}_2\right) f_1^1\left(\mathbf{q}_1\right) \right] . \end{aligned} \quad (80)$$

The reduced vertices $\left(\mathbf{V}_{\ell_1 m_1; \ell_2 m_2}^\alpha\right)_\ell^m$ are obtained from (59) (60), (55) and (56). We do not

present them explicitly, but discuss qualitatively their φ - and T-dependence. For this it is

important to notice that $\left(\mathbf{V}_{\ell_1 m_1; \ell_2 m_2}^\alpha\right)_\ell^m$ involve $c_{\ell_1}^{m_1}\left(\mathbf{q}_1\right) c_{\ell_2}^{m_2}\left(\mathbf{q}_2\right)$. Fixing φ ($0 < \varphi < 1$) one

finds from (68)-(73) that

$$c_0^0\left(\mathbf{q};\varphi,T\right) \rightarrow c_0^0\left(\mathbf{q};\varphi\right) \neq 0$$

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

for T (or T^*) $\rightarrow \infty$. Therefore, for $T = \infty$ the functional $\left(\int_0^T \right)_0^0$ reduces to that for simple hard spheres, as it is expected. In this case there is a dynamic transition (Type-B) at a critical packing fraction $\varphi_c \cong 0.51 - 0.52$ [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 the eqs. (77)-(80) for given φ 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) takes place, respectively. Three different transition scenarios are possible: for $T_1^* \cong 0.32 < T^* \leq \infty$ the TDOF freeze at $\varphi_c \cong 0.52$ into a nonergodic phase (type-B) whereas the ODOF remain ergodic for all φ . Note that T_1^* is the value on the type-A transition line for $\varphi_{RCP} = 0.64$, the packing fraction for random close packing. Since larger values than φ_{RCP} are unphysical, we have used φ_{RCP} as a cutoff. In addition we stress that the accuracy of T_1^* should not be overestimated, because the Percus-Yevick approximation for hard spheres does not describe correctly the singularity which is expected for $\varphi = \varphi_{RCP}$. Hence, this approximation becomes worse by approaching φ_{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 φ 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 ten percent, due to the flatness of the critical lines in the vicinity of T_2^* . For $T^* < T_2^*$, both, TDOF and ODOF freeze simultaneously at the critical line $\varphi_c^B(T)$ (type-B) (solid line for $T^* < T_2^*$).

Figures 2a-4a represent the critical non-ergodicity parameters $f_\ell^{m,c}(y)$ and figures 2b-4b the corresponding static correlators $S_\ell^m(y)$ for three different points on $\phi_c^B(T)$ for $T^* < T_2^*$. Comparison of both sets of figures shows that the q-dependence (y-dependence) of $f_\ell^{m,c}$ is in phase with the q-dependence of S_ℓ^m . Hence, we find the similar behaviour for $(\ell,m) \neq (0,0)$ as already found for simple liquids, i.e. for $(\ell,m) = (0,0)$ [1]. Furthermore, we point out the strong m-dependence of $f_1^{m,c}(y)$, even for $y = 0$. Since the form factors $f_\ell^{m,c}(y)$ increases uniformly when moving on $\phi_c^B(T)$ towards $T \rightarrow 0$, the TDOF and ODOF 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 non-ergodicity parameter $f_1(q)$ follows from

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

$f_1^c(q)$ is presented in figure 5 for three different points on $\phi_c^B(T)$ for $T^* < T_2^*$. $f_1^c(q)$ gives the strength of the α -relaxation for $T > T_c(\phi)$ (ϕ fixed), i.e. the area under the α -peak of the imaginary part $\chi_{\ell=1}^{(0)''}(q, \omega)$ of the corresponding susceptibility $\chi_{\ell=1}^{(0)}(q, \omega)$ as a function of $\ell n \omega$ is $f_1^c(q)$ [1]. The superscript (0) indicates the susceptibility (for $\ell = 1$) 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 figure 5) the minimum between the α -peak and the microscopic or Boson peak might be rather shallow for $\chi_{\ell=1}^{(0)''}(0, \omega)$ compared to $\chi_{\ell=0}''(0, \omega)$ (see also the discussion of that point in section 5).

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

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

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

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

Making use of the fluctuation dissipation theorem and the relationship between $\chi_{ij}^{(0)}$ and

$\left(\chi^{(0)}\right)_1^m$ one gets:

$$\epsilon''(\omega) = \left(\chi^{(0)}\right)_1^{1''}(q = 0, \omega) = \frac{1}{2} \omega \lim_{q \rightarrow 0} \tilde{S}_1^1(q, \omega) / S_1^1(q) \quad . \quad (86)$$

where $\tilde{S}_\ell^m(q, \omega)$ is the Fourier transform of $S_\ell^m(q, t)$ and $\left(\chi^{(0)}\right)_\ell^{m''}(q, \omega)$ the imaginary part of the corresponding (normalized) susceptibility.

The reader should note that the inequality (85) implies that $\tilde{S}_1^m(0, \omega)$ and therefore $S_1^m(0, t)$, too, depends on m . This can be observed for $t = 0$ from Figures 3b and 4b and can be proven

with the explicit result for $c_\ell^m(\mathbf{q})$ in appendix E. A similar relationship as (86), holds for the imaginary part $\kappa''(\mathbf{q}\mathbf{e}_3, \omega)$ of the compressibility:

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

Again, the area under the α -peak of $\chi_\ell^{m''}(\mathbf{q}\mathbf{e}_3, \omega)$ as function of $\ell n\omega$ is about $f_\ell^{m,c}(\mathbf{q})$. From Figs. 2a and 4a we obtain:

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

for the three points on the critical line $\eta_c^B(T)$. q_1 is the position of the first maximum of $S_0^0(\mathbf{q})$. For instance, it is $f_1^{1,c}(\mathbf{q}=0) \approx 2f_0^{0,c}(\mathbf{q}=q_1)$ for the point with highest temperature. Therefore, the strength of the α -process (normalized to the static susceptibility) obtained from the dielectric measurement (which is at $\mathbf{q}=0$!) is about twice as large as that which will follow from neutron scattering at $\mathbf{q}=q_1$.

5. Discussion and conclusions

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

We have demonstrated that the choice of $j_{\ell m}^T(\vec{q})$ and $j_{\ell m}^R(\vec{q})$, besides $\delta\rho_{\ell m}(\vec{q})$, 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 have performed for the static three-point correlator, one ends up with expressions for the vertices of the mode coupling polynomial which are in close relationship to those for simple liquids [1]-[3].

The resulting MCT-equations for the non-ergodicity parameter were solved for a system of dipolar hard spheres. Making use of the static correlators in mean spherical and Percus-Yevick approximation and restriction to $\alpha = 0, 1$, the η - T -phase diagram has been determined. For this we have also assumed diagonality of the memory kernel with respect to α and α' . Taking also $m_{\lambda\lambda}^{\text{RT}}(\mathbf{q}, t)$ into account, does not change the topology of the phase diagram, but shifts the phase boundaries towards higher temperatures [47]. The main conclusion which can be drawn is the existence of three different transition scenarios which are:

(i) only the TDOF freeze, whereas the ODOF remain "liquid". This happens for all ϕ with $\phi_c \cong 0.52 \leq \phi < \phi_{\text{RCP}}$, provided $T_1 < T \leq \infty$. In this temperature range there is *no* influence of the dipolar interactions. The non-ergodicity parameter $f_0^0(\mathbf{q}; \phi, T)$ is T -independent and its q - and ϕ -dependence is identical to that for the hard sphere system, without dipoles.

(ii) if $T_2 \leq T \leq T_1$, the TDOF freeze first at $\phi_c \cong 0.52$ via a type-B transition, and at the critical line $\phi_c^{\text{A}}(T)$ (dashed line in figure 1) the ODOF freeze by a type-A transition. This latter transition corresponds to a *spin glass transition* [48], as it was discussed within MCT for Heisenberg spin glasses by Götze and Sjögren [49].

(iii) for $T < T_2$ both, TDOF and ODOF, freeze simultaneously at the critical line $\phi_c^{\text{B}}(T)$.

These findings demonstrate a hierarchy for the freezing, i.e. the ODOF can never freeze before the TDOF are frozen. This result becomes obvious from (80). Assuming

$f_0^0(\mathbf{q}) \equiv 0$, it follows that $\left(\mathcal{H}^{\alpha}\right)_1^m \equiv 0$, which implies that $f_1^m(\mathbf{q}) \equiv 0$. A freezing of the

ODOF alone, could only occur if $\left(\mathcal{H}^{\alpha}\right)_1^m$ would involve a term $f_1^m(\mathbf{q}_1)f_1^m(\mathbf{q}_2)$. Such a

term, however, is forbidden due to the parity rule which requires $l_1 + l_2$ 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 α to 0 and 1 nor of the approximation of the static three-point correlator (cf. eq. (C.6)), but a result of the additional symmetry of dipolar hard spheres, which is the invariance under the

transformation $\{\mu_n\} \rightarrow \{-\mu_n\}$. This symmetry implies that $S_{\ell_m, \ell'_m}(\mathbf{q}, t)$ and therefore $f_{\ell_m, \ell'_m}(\mathbf{q})$, too, and $M_{\ell_m, \ell'_m}^{\alpha\alpha'}(\mathbf{q}, t)$ vanish, if $\ell + \ell'$ is odd. Consequently, ℓ and ℓ' must be both either even or odd. Let us symbolically denote $f_{\ell_m, \ell'_m}(\mathbf{q})$ by $f_{\text{even}}(\mathbf{q})$ and $f_{\text{odd}}(\mathbf{q})$ for ℓ, ℓ' even and ℓ, ℓ' odd, respectively, and similarly for $M_{\ell_m, \ell'_m}^{\alpha\alpha'}(\mathbf{q}, t)$. Then, the equation for f_{even} involves $M_{\text{even}}^{\alpha\alpha'}$ and that for f_{odd} involves $M_{\text{odd}}^{\alpha\alpha'}$, only. Taking further into account that the vertices of $M_{\ell_m, \ell'_m}^{\alpha\alpha'}$ vanish for $\ell_1 + \ell_2$ odd and/or $\ell_3 + \ell_4$ 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_{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 (i.e. $\mu = 0$) induces a glass transition for all f_{ℓ_m, 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} for ℓ_o, ℓ'_o odd freezes, then all ODOF with ℓ and ℓ' odd will freeze. Therefore, the different transition scenarios described above do not really discriminate between TDOF and ODOF, 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. The temperature (as far as the density remains constant) seems to play a less important role.

With the behaviour 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 extra-

polation of the steep descent of $\phi_c^B(T)$ depicted in figure 1 would suggest the existence of such a finite temperature, one can prove that $\phi_c^B(T) \rightarrow 0$ for $T \rightarrow 0$. In this respect we would like to mention that a similar steep descent of $\phi_c^B(T)$ has been found by Lai and Chang [51] for a system of *charged* hard spheres.

The variation of the non-ergodicity parameters $f_\ell^{m,c}(q)$ (on the critical type-B line) in phase with $S_\ell^m(q)$ is similar to the behaviour found for simple liquids [1]. Comparison of figure 2a and 4a 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 $\phi_c^B(T)$ we have investigated. This implies that the spectral weight of the "normalized" α -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 $\phi_c^B(T)$. The reason for this behaviour is as follows: comparison of Figs. 2b and 4b 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 α -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. This may stress the importance of the dipolar interactions for the conclusions with respect to the relaxation strength of the α -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.

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Figure captions

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

Fig.2: The critical non-ergodicity parameter (a) and the static correlator (b) for $\beta = 0$, $m = 0$ and three different points for (T^*, ϕ) on the critical line $\phi_c^B(T)$ as a function of $y = qd$.

Fig.3: Same as figure 2, but for $\beta = 1$, $m = 0$.

Fig.4: Same as figure 2, but for $\beta = 1$, $m = 1$.

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

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Appendix A: Calculation of $J_{\lambda_1\lambda_2}^{\alpha_1\alpha_2}(\mathbf{q})$

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

$$J_{\lambda_1\lambda_2}^{\alpha_1\alpha_2}(\mathbf{q}) = \frac{1}{N} \left(q_{\ell_1}^{\alpha_1}(\mathbf{q}) q_{\ell_2}^{\alpha_2}(\mathbf{q}) \right)^{-1} \cdot \sum_{n_1 n_2} \sum_{k_1 k_2} \left\langle v_{n_1}^{\alpha_1 k_1} \left(\hat{q}^{\alpha_1 k_1} \rho_{n_1} \right)_{\lambda_1}(\mathbf{q}) * v_{n_2}^{\alpha_2 k_2} \left(\hat{q}^{\alpha_2 k_2} \rho_{n_2} \right)_{\lambda_2}(\mathbf{q}) \right\rangle \quad (\text{A.1})$$

where we introduced:

$$\rho_{n,\lambda}(\mathbf{q}) = \sqrt{4\pi i}^\ell e^{i\mathbf{q}\mathbf{x}_n} Y_{\ell m}(\Omega_n) \quad , \quad \lambda = (\ell, m) \quad (\text{A.2})$$

Since

$$\left\langle v_{n_1}^{\alpha_1 k_1} v_{n_2}^{\alpha_2 k_2} \dots \right\rangle = \left\langle v_{n_1}^{\alpha_1 k_1} v_{n_2}^{\alpha_2 k_2} \right\rangle \langle \dots \rangle \quad (\text{A.3})$$

$$= \frac{kT}{I_{\alpha_1}} \delta_{\alpha_1 \alpha_2} \delta_{k_1 k_2} \delta_{n_1 n_2} \langle \dots \rangle$$

it follows

$$J_{\lambda_1\lambda_2}^{\alpha_1\alpha_2}(\mathbf{q}) = \frac{1}{N} \left(q_{\ell_1}^{\alpha_1}(\mathbf{q}) q_{\ell_2}^{\alpha_1}(\mathbf{q}) \right)^{-1} \delta_{\alpha_1 \alpha_2} \frac{kT}{I_{\alpha_1}} \cdot$$

(A.4)

$$\cdot \sum_n \left\langle \left(\hat{\mathbf{q}}^{\alpha_1} \rho_n \right)_{\lambda_1} (\mathbf{q})^* \left(\hat{\mathbf{q}}^{\alpha_1} \rho_n \right)_{\lambda_2} (\mathbf{q}) \right\rangle$$

Here a comment is in order. To derive (A.3) for $\alpha_1 = \alpha_2 = \mathbf{R}$ it is important to use the angular velocity $\dot{\omega}_n$ and the angular momentum operator \mathbf{L}' in the body fixed frame (where $\dot{L}_3 = (\mathbf{R}(\phi, \theta) \mathbf{L})_3 = 0$) because only then $\exp(-\beta H)$ factorizes into a kinetic and a potential part where the kinetic term only involves $\dot{\omega}_n$ [34]. After having performed the averaging over $\{\dot{\omega}_n\}$ one may transform back to the laboratory fixed frame. For $\alpha = \mathbf{T}$ and $\alpha' = \mathbf{R}$, or vice versa, it is obvious that the correlator must vanish, since $\left\langle v_{n_1}^{\text{Tk}_1} v_{n_2}^{\text{Rk}_2} \dots \right\rangle = \left\langle v_{n_1}^{\text{Tk}_1} \right\rangle \left\langle v_{n_2}^{\text{Rk}_2} \right\rangle \dots = 0$, due to $\left\langle v_{n_1}^{\text{Tk}_1} \right\rangle = 0$.

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

$$\exp[-i(\mathbf{q}_1 - \mathbf{q}_2) \cdot \mathbf{x}_n] Y_{\ell_1 m_1}^*(\Omega_n) Y_{\ell_2 m_2}(\Omega_n)$$

$= \exp[-i(\mathbf{q}_1 - \mathbf{q}_2) \cdot \mathbf{x}_n] (-1)^{m_1} Y_{\ell_1 - m_1}(\Omega_n) Y_{\ell_2 m_2}(\Omega_n)$. Therefore, it is

$$\left(\hat{\mathbf{q}}^{\alpha} \rho_n \right)_{\lambda_1} (\mathbf{q}_1)^* \left(\hat{\mathbf{q}}^{\alpha} \rho_n \right)_{\lambda_2} (\mathbf{q}_2)$$

$$= (-1)^{m_1} \sum_{\lambda} C(\ell_1 \ell_2 \ell; -m_1 m_2 m) a_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}_1 \mathbf{q}_2) \sqrt{4\pi} (-i)^{\ell} e^{-i(\mathbf{q}_1 - \mathbf{q}_2) \cdot \mathbf{x}_n} Y_{\ell m}(\Omega_n)$$

(A.5)

$$= (-1)^{m_2} \sum_{\lambda} C(\ell_1 \ell_2 \ell; -m_1 m_2 m) a_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}_1 \mathbf{q}_2) \rho_{n, \lambda}^*(\mathbf{q}_1 - \mathbf{q}_2)$$

where $a_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}_1 \mathbf{q}_2)$, which depends on ℓ_1, ℓ_2, ℓ and $(\mathbf{q}_1 \cdot \mathbf{q}_2)$ only, takes into account that the

l.h.s. of (A.5) is not normalized. With the scalar product

$$\begin{aligned}
(\rho_{n,\lambda}(\mathbf{q}), \rho_{n,\lambda'}(\mathbf{q}')) &= \frac{1}{4\pi V} \int_V d^3 x_n \int d^2 \Omega_n \rho_{n,\lambda}(\mathbf{q})^* \rho_{n,\lambda'}(\mathbf{q}') \\
&= \delta_{\mathbf{q},\mathbf{q}'} \delta_{\lambda,\lambda'},
\end{aligned} \tag{A.6}$$

we immediately obtain from (A.5)

$$a_{\ell_1 \ell_2 \ell}^\alpha(\mathbf{q}_1 \mathbf{q}_2) = (C(\ell_1 \ell_2 \ell; 000))^{-1} \left(\left(\hat{\mathbf{q}}^\alpha \rho_n \right)_{\ell_1 0}(\mathbf{q}_1) \left(\hat{\mathbf{q}}^\alpha \rho_n \right)_{\ell_2 0}(\mathbf{q}_2)^* \rho_{n,\ell 0}(\mathbf{q}_1 - \mathbf{q}_2) \right) \tag{A.7}$$

where a straightforward calculation, which uses the product rule for $Y_{\ell m}$ [34], yields with (22), (A.2) and (A.6)

$$a_{\ell_1 \ell_2 \ell}^\alpha(\mathbf{q}_1 \mathbf{q}_2) = i^{\ell + \ell_2 - \ell_1} \left(\frac{(2\ell_1 + 1)(2\ell_2 + 1)}{2\ell + 1} \right)^{\frac{1}{2}} \bullet \tag{A.8}$$

$$\bullet \begin{cases} \mathbf{q}_1 \mathbf{q}_2 C(\ell_1 \ell_2 \ell; 000) & , \quad \alpha = T \\ \left(\ell_1 (\ell_1 + 1) \ell_2 (\ell_2 + 1) \right)^{\frac{1}{2}} \left(-\frac{1}{2} \right) \left[C(\ell_1 \ell_2 \ell; 1-10) + C(\ell_1 \ell_2 \ell; 110) \right] & , \quad \alpha = R \end{cases}$$

Eq. (A.5) together with (A.8) is the basic result, which will be used in the following.

Since it is

$$\langle \rho_{n,\lambda}(\mathbf{q}) \rangle = \delta_{\mathbf{q},0} \delta_{\lambda,0} \quad , \tag{A.9}$$

we get with (A.5), (A.8) and $C(\ell_1 \ell_2 0; m_1 m_2 0)$ from ref. [34] that

$$\left\langle \left(\hat{\mathbf{q}}^{\alpha_1 \rho_n} \right)_{\lambda_1} (\mathbf{q}) * \left(\hat{\mathbf{q}}^{\alpha_1 \rho_n} \right)_{\lambda_2} (\mathbf{q}) \right\rangle = \delta_{\lambda_1, \lambda_2} \left(\mathbf{q}_{\ell_1}^{\alpha_1} (\mathbf{q}) \right)^2 \quad (\text{A.10})$$

with $\mathbf{q}_\ell^\alpha (\mathbf{q})$ from (37). Substituting (A.10) into (A.4) finally yields:

$$J_{\lambda_1 \lambda_2}^{\alpha_1 \alpha_2} (\mathbf{q}) = \frac{kT}{I_{\alpha_1}} \delta_{\lambda_1, \lambda_2} \delta_{\alpha_1, \alpha_2} \quad (\text{A.11})$$

for all \mathbf{q} .

Appendix B: Calculation of $\left\langle \ell j_\lambda^\alpha (\mathbf{q}) * Q | \delta \rho_{\lambda_1} (\mathbf{q}_1) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle$

Substitution of $Q = 1 - P$ leads to:

$$\begin{aligned} & \left\langle \ell j_\lambda^\alpha (\mathbf{q}) * Q | \delta \rho_{\lambda_1} (\mathbf{q}_1) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle \\ &= \left\langle \ell j_\lambda^\alpha (\mathbf{q}) * | \delta \rho_{\lambda_1} (\mathbf{q}_1) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle - \left\langle \ell j_\lambda^\alpha (\mathbf{q}) * P | \delta \rho_{\lambda_1} (\mathbf{q}_1) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle \end{aligned} \quad (\text{B.1})$$

(i) Let us first calculate $\left\langle \ell j_\lambda^\alpha (\mathbf{q}) * | \delta \rho_{\lambda_1} (\mathbf{q}_1) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle$. Because ℓ is hermitean, it is:

$$\begin{aligned} & \left\langle \ell j_\lambda^\alpha (\mathbf{q}) * | \delta \rho_{\lambda_1} (\mathbf{q}_1) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle = \left\langle j_\lambda^\alpha (\mathbf{q}) * | (\ell \delta \rho_{\lambda_1} (\mathbf{q}_1)) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle + (1 \leftrightarrow 2) \\ &= \left(\mathbf{q}_\ell^\alpha (\mathbf{q}) \right)^{-1} \sum_{\alpha_1} \left\langle \left(\hat{\mathbf{q}}^{\alpha} \mathbf{j}^\alpha \right)_\lambda (\mathbf{q}) * \left(\hat{\mathbf{q}}^{\alpha_1} \mathbf{j}^{\alpha_1} \right)_{\lambda_1} (\mathbf{q}_1) \delta \rho_{\lambda_2} (\mathbf{q}_2) \right\rangle + (1 \leftrightarrow 2) \end{aligned} \quad (\text{B.2})$$

where (20) and (36) was used. Substituting $\mathbf{j}_\lambda^\alpha(\mathbf{q})$ from (17) into (B.2) and performing the average over the velocities (cf. appendix A) we get with (A.2):

$$\left\langle \mathbf{j}_\lambda^\alpha(\mathbf{q})^* |\delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2)\right\rangle = \frac{kT}{I_\alpha} \left(\mathbf{q}_\ell^\alpha(\mathbf{q}) \right)^{-1} \sum_n \left\langle \left(\hat{\mathbf{q}}_{\rho_n}^\alpha \right)_\lambda(\mathbf{q})^* \left(\hat{\mathbf{q}}_{\rho_n}^\alpha \right)_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle + (1 \leftrightarrow 2) \quad (\text{B.3})$$

Now, eq. (A.5) can be used. This yields

$$\begin{aligned} & \left\langle \mathbf{j}_\lambda^\alpha(\mathbf{q})^* |\delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2)\right\rangle \\ &= \frac{kT}{I_\alpha} \left(\mathbf{q}_\ell^\alpha(\mathbf{q}) \right)^{-1} (-1)^{m_1} \sum_{\lambda_2} C\left(\ell\ell_1\ell_2; -m\ m_1 - m_2\right) a_{\ell\ell_1\ell_2}^\alpha(\mathbf{q}\mathbf{q}_1) \cdot \\ & \left\langle \sum_n \rho_{n,\lambda_2}^*(\mathbf{q} - \mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle \\ &+ (1 \leftrightarrow 2) \end{aligned}$$

For the next step we notice that

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

and with some properties of $C(\ell_1 \ell_2 \ell; m_1 m_2 m)$ [34] we find that

$$(-1)^{m_1} C\left(\ell\ell_1\ell_2; -m\ m_1 m_2\right) a_{\ell\ell_1\ell_2}^\alpha = \mathbf{q}_\ell^\alpha(\mathbf{q}) b_{\ell_1\ell_2\ell}^\alpha(\mathbf{q}\mathbf{q}_1) C\left(\ell_1\ell_2\ell; m_1 m_2 m\right)$$

with $b_{\ell_1\ell_2\ell}^\alpha(\mathbf{q}\mathbf{q}_1)$ from eq. (56). Putting this together we arrive at

$$\left\langle \mathbf{j}_\lambda^\alpha(\mathbf{q})^* |\delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2)\right\rangle = N\delta_{\mathbf{q},\mathbf{q}_1+\mathbf{q}_2} \frac{kT}{I_\alpha} \quad . \quad (\text{B.4})$$

$$\begin{aligned}
& \cdot \sum_{\lambda_2} b_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1) \mathbf{C}(\ell_1 \ell_2 \ell; \mathbf{m}_1 \mathbf{m}_2 \mathbf{m}) \mathbf{S}_{\lambda_2 \lambda_2}(\mathbf{q}_2) + (1 \leftrightarrow 2) \\
& = N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \frac{kT}{I_\alpha} \sum_{\lambda_1 \lambda_2 \lambda} b_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1) \mathbf{C}(\ell_1 \ell_2 \ell; \mathbf{m}_1 \mathbf{m}_2 \mathbf{m}) \left(\mathbf{S}^{-1}(\mathbf{q}_1) \right)_{\lambda_1 \lambda} \mathbf{S}_{\lambda \lambda_1}(\mathbf{q}_1) \cdot \\
& \quad \cdot \mathbf{S}_{\lambda_2 \lambda_2}(\mathbf{q}_2) + (1 \leftrightarrow 2)
\end{aligned}$$

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

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

it follows:

$$\begin{aligned}
\left\langle \mathcal{L} j_{\lambda}^{\alpha}(\mathbf{q}) * |\delta \rho_{\lambda_1}(\mathbf{q}_1) \delta \rho_{\lambda_2}(\mathbf{q}_2)| \right\rangle &= N \delta_{\mathbf{q}, \mathbf{q}_1 + \mathbf{q}_2} \frac{kT}{I_\alpha}. \tag{B.5} \\
& \left\{ \sum_{\lambda_1 \lambda_2} \left[b_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1) \mathbf{C}(\ell_1 \ell_2 \ell; \mathbf{m}_1 \mathbf{m}_2 \mathbf{m}) + (1 \leftrightarrow 2) \right] \mathbf{S}_{\lambda_1 \lambda_1}(\mathbf{q}_1) \mathbf{S}_{\lambda_2 \lambda_2}(\mathbf{q}_2) - \right. \\
& \left. - \frac{\rho_0}{4\pi} \sum_{\lambda_1 \lambda_2 \lambda} \left[b_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1) \mathbf{C}(\ell_1 \ell_2 \ell; \mathbf{m}_1 \mathbf{m}_2 \mathbf{m}) c_{\lambda \lambda}(\mathbf{q}_1) \mathbf{S}_{\lambda \lambda_1}(\mathbf{q}_1) \mathbf{S}_{\lambda_2 \lambda_2}(\mathbf{q}_2) + (1 \leftrightarrow 2) \right] \right\}.
\end{aligned}$$

Substituting $b_{\ell_1 \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1)$ from (56) and making use of

$$\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q} \tag{B.6}$$

and

$$\sqrt{\ell_1(\ell_1+1)}C(\ell_1\ell_2\ell;101)+\sqrt{\ell_2(\ell_2+1)}C(\ell_1\ell_2\ell;011)=\sqrt{\ell(\ell+1)}C(\ell_1\ell_2\ell;000) \quad (\text{B.7})$$

one can prove by use of the properties of $C(\ell_1\ell_2\ell; m_1m_2m)$ [34] that

$$\left[b_{\ell_1\ell_2\ell}^{\alpha}(\mathbf{q}\mathbf{q}_1)C(\ell_1\ell_2\ell; m_1m_2m) + (1 \leftrightarrow 2) \right] = q_{\ell}^{\alpha}(\mathbf{q}) b_{\ell_1\ell_2\ell} C(\ell_1\ell_2\ell; m_1m_2m) \quad (\text{B.8})$$

with

$$b_{\ell_1\ell_2\ell}^{\alpha} = (-i)^{\ell} i^{\ell_1+\ell_2} \left(\frac{(2\ell_1+1)(2\ell_2+1)}{2\ell+1} \right)^{\frac{1}{2}} c(\ell_1\ell_2\ell; 000) \quad (\text{B.9})$$

(ii) With $P = P_p + P_j$ from (38) and (39) we obtain for the second term of (B.1)

$$\begin{aligned} \left\langle \mathcal{L}j_{\lambda}^{\alpha}(\mathbf{q})^* P |\delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle &= \frac{1}{N} \sum_{\lambda_1\lambda_2} \left(\mathbf{S}^{-1}(\mathbf{q}) \right)_{\lambda_1\lambda_2} \left\langle \mathcal{L}j_{\lambda}^{\alpha}(\mathbf{q})^* |\delta\rho_{\lambda_1}(\mathbf{q}) \right\rangle \\ &\quad \left\langle \delta\rho_{\lambda_2}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle \\ &= \frac{1}{N} \sum_{\lambda_1\lambda_2} \left(\mathbf{S}^{-1}(\mathbf{q}) \right)_{\lambda_1\lambda_2} \sum_{\alpha_1} \left\langle j_{\lambda}^{\alpha}(\mathbf{q})^* j_{\lambda_1}^{\alpha_1}(\mathbf{q}) \right\rangle \left\langle \delta\rho_{\lambda_2}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle \\ &= \frac{kT}{I_{\alpha}} \sum_{\lambda_2} \left(\mathbf{S}^{-1}(\mathbf{q}) \right)_{\lambda\lambda_2} \left\langle \delta\rho_{\lambda_2}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle \end{aligned} \quad (\text{B.10})$$

where we used again the hermiticity of \mathcal{L} and eqs. (20) and (40). Unfortunately, the static three-point correlator in (B.10) cannot be calculated exactly. In Appendix C it will be shown that it can be approximated as follows:

$$\left\langle \delta\rho_{\lambda_2}(\mathbf{q})^* \delta\rho_{\lambda_1}(\mathbf{q}_1)\delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle$$

$$\approx N\delta_{\mathbf{q},\mathbf{q}_1+\mathbf{q}_2} \sum_{\lambda_1\lambda_2\lambda_3} b_{\ell_1\ell_2\ell_3} C\left(\ell_1\ell_2\ell_3; m_1m_2m_3\right) S_{\lambda_2\lambda_3}(\mathbf{q}) S_{\lambda_1\lambda_1}(\mathbf{q}_1) S_{\lambda_2\lambda_2}(\mathbf{q}_2)$$

With this, we get from (B.10):

$$\begin{aligned} & \left\langle \ell_j^\alpha(\mathbf{q}) * P | \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \right\rangle \quad (\text{B.11}) \\ & \approx N\delta_{\mathbf{q},\mathbf{q}_1+\mathbf{q}_2} \frac{kT}{I_\alpha} \sum_{\lambda_1\lambda_2} b_{\ell_1\ell_2\ell} C\left(\ell_1\ell_2\ell; m_1m_2m\right) S_{\lambda_1\lambda_1}(\mathbf{q}_1) S_{\lambda_2\lambda_2}(\mathbf{q}_2). \end{aligned}$$

If we use (B.8), the first term in the curly bracket of (B.5) (including the prefactor) just cancels the second term (B.11) of (B.1). What remains for (B.1) is the second term in the curly bracket which coincides with (54).

Appendix C: Approximation of $\left\langle \delta\rho_{\lambda_1}(\mathbf{q}_1) * \delta\rho_{\lambda_2}(\mathbf{q}_2) \delta\rho_{\lambda_3}(\mathbf{q}_3) \right\rangle$

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

$$\left\langle \delta\rho(\mathbf{q}_1) * \delta\rho(\mathbf{q}_2) \delta\rho(\mathbf{q}_3) \right\rangle \approx N\delta_{\mathbf{q}_1,\mathbf{q}_2+\mathbf{q}_3} S(\mathbf{q}_1) S(\mathbf{q}_2) S(\mathbf{q}_3) \quad (\text{C.1})$$

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 (C.1) for $\lambda_1 = \lambda_2 = \lambda_3 = (0,0)$. We choose the following approximation:

$$\left\langle \delta\rho_{\lambda_1}(\mathbf{q}_1) * \delta\rho_{\lambda_2}(\mathbf{q}_2) \delta\rho_{\lambda_3}(\mathbf{q}_3) \right\rangle =$$

$$\begin{aligned}
&= (4\pi)^{3/2} i^{\ell_2+\ell_3-\ell_1} \int \prod_{j=1}^3 d^2 \Omega_j \langle \delta\rho(\mathbf{q}_1, \Omega_1) * \delta\rho(\mathbf{q}_2, \Omega_2) \delta\rho(\mathbf{q}_3, \Omega_3) \rangle Y_{\lambda_1}^*(\Omega_1) Y_{\lambda_2}(\Omega_2) Y_{\lambda_3}(\Omega_3) \\
&\approx i^{\ell_2+\ell_3-\ell_1} (4\pi)^{3/2} (4\pi/N)^2 \int \prod_j \left(d^2 \Omega_j d^2 \Omega'_j \right) \int d^2 \Omega \Pi \delta(\Omega, \Omega'_j) Y_{\lambda_1}^*(\Omega_1) Y_{\lambda_2}(\Omega_2) Y_{\lambda_3}(\Omega_3) \cdot \\
&\quad \cdot \left\langle \delta\rho(\mathbf{q}_1, \Omega_1) * \delta\rho(\mathbf{q}_1, \Omega'_1) \delta\rho(\mathbf{q}_2, \Omega_2) \delta\rho(\mathbf{q}_2, \Omega'_2) * \delta\rho(\mathbf{q}_3, \Omega_3) \delta\rho(\mathbf{q}_3, \Omega'_3) * \right\rangle
\end{aligned}$$

Factorization of the six-point correlator

$$\begin{aligned}
&\left\langle \delta\rho(\mathbf{q}_1, \Omega_1) * \delta\rho(\mathbf{q}_1, \Omega'_1) \delta\rho(\mathbf{q}_2, \Omega_2) \delta\rho(\mathbf{q}_2, \Omega'_2) * \delta\rho(\mathbf{q}_3, \Omega_3) \delta\rho(\mathbf{q}_3, \Omega'_3) * \right\rangle \\
&\quad (C.2) \\
&\approx N^3 S(\mathbf{q}_1, \Omega_1, \Omega'_1) S(\mathbf{q}_2, \Omega_2, \Omega'_2) * S(\mathbf{q}_3, \Omega_3, \Omega'_3) * \delta_{\mathbf{q}_1, \mathbf{q}_2+\mathbf{q}_3}
\end{aligned}$$

where

$$S(\mathbf{q}, \Omega, \Omega') = \frac{1}{N} \langle \delta\rho(\mathbf{q}, \Omega) * \delta\rho(\mathbf{q}, \Omega') \rangle \quad (C.3)$$

and using that

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

$$\int d^2 \Omega \Pi \delta(\Omega, \Omega'_j) = (4\pi)^{-1/2} \sum_{\substack{\lambda_1 \lambda_2 \lambda_3 \\ \ell_1 \ell_2 \ell_3}} b_{\lambda_1 \lambda_2 \lambda_3} c\left(\begin{matrix} \ell_1 \ell_2 \ell_3 \\ m_1 m_2 m_3 \end{matrix}\right) \cdot$$

$$\cdot Y_{\lambda_1}(\Omega'_1) Y_{\lambda_2}^*(\Omega_2) Y_{\lambda_3}^*(\Omega_3) \quad (C.5)$$

leads to

$$\langle \delta\rho_{\lambda_1}(\mathbf{q}_1) \delta\rho_{\lambda_2}(\mathbf{q}_2) \delta\rho_{\lambda_3}(\mathbf{q}_3) \rangle \quad (\text{C.6})$$

$$\approx N\delta_{\mathbf{q},\mathbf{q}_1+\mathbf{q}_2} \sum_{\lambda_1\lambda_2\lambda_3} b_{\ell_1\ell_2\ell_3} C\left(\begin{matrix} \ell_1 & \ell_2 & \ell_3 \\ m_1 & m_2 & m_3 \end{matrix}; \lambda_1\lambda_1, \lambda_2\lambda_2, \lambda_3\lambda_3\right) S_{\lambda_1\lambda_1}(\mathbf{q}_1) S_{\lambda_2\lambda_2}(\mathbf{q}_2) S_{\lambda_3\lambda_3}(\mathbf{q}_3)$$

which is the result we used in appendix B. It is easy to prove that (C.6) reduces to (C.1) 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 $\mathbf{q} \rightarrow 0$

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

$$\mathbf{q}_2 = \mathbf{q}_1 (-1 + \mathbf{q} \cdot \boldsymbol{\varepsilon}) \quad , \quad |\boldsymbol{\varepsilon}| = 0(1) \quad (\text{D.1})$$

Then, we obtain with

$$\begin{aligned} c_{\lambda\lambda}(\mathbf{q}_2) &= c_{\lambda\lambda}(-\mathbf{q}_1) + 0(\mathbf{q}) \\ &= (-1)^{\ell+\ell'+m+m'} c_{\bar{\lambda}\bar{\lambda}}(\mathbf{q}_1) + 0(\mathbf{q}) \quad , \end{aligned} \quad (\text{D.2})$$

where (24) and (25) (which also hold for $c_{\lambda\lambda}(\mathbf{q})$) and $\bar{\lambda} = (\ell, -m)$ were used, that

$$\begin{aligned} \sum_{\lambda''} v^{\alpha}(\mathbf{q}, \lambda | \mathbf{q}_1 \lambda_1; \mathbf{q}_2 \lambda_2; \lambda'') &= \\ &= \sum_{\lambda} \left[b_{\ell \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1) C\left(\begin{matrix} \ell & \ell_2 & \ell \\ m & m_2 & m \end{matrix}\right) c_{\lambda''\lambda_1}(\mathbf{q}_1) + \right. \end{aligned}$$

$$\begin{aligned}
& +(-1)^{\ell_2+\ell''+m_2+m''} b_{\ell \ell_1 \ell}^{\alpha}(-\mathbf{q}\mathbf{q}_1)C\left(\begin{matrix} \ell & \ell_1 & \ell \\ m & m_1 & m \end{matrix}\right)c_{\bar{\lambda}_2 \bar{\lambda}''}(\mathbf{q}_1)] + 0(\mathbf{q}) \\
& = \sum_{\lambda'' (\neq \bar{\lambda}_2)} b_{\ell \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1)C\left(\begin{matrix} \ell & \ell_2 & \ell \\ m & m_2 & m \end{matrix}\right)c_{\lambda'' \lambda_1}(\mathbf{q}_1) \\
& + \sum_{\lambda'' (\neq \bar{\lambda}_1)} (-1)^{\ell_2+\ell''+m_2+m''} b_{\ell \ell_1 \ell}^{\alpha}(-\mathbf{q}\mathbf{q}_1)C\left(\begin{matrix} \ell & \ell_1 & \ell \\ m & m_1 & m \end{matrix}\right)c_{\bar{\lambda}_2 \bar{\lambda}''}(\mathbf{q}_1) \\
& + \left[b_{\ell_2 \ell_2 \ell}^{\alpha}(\mathbf{q}\mathbf{q}_1)C\left(\begin{matrix} \ell_2 & \ell_2 & \ell \\ -m_2 & m_2 & m \end{matrix}\right) + (-1)^{\ell_1+\ell_2+m_1+m_2} b_{\ell_1 \ell_1 \ell}^{\alpha}(-\mathbf{q}\mathbf{q}_1)C\left(\begin{matrix} \ell_1 & \ell_1 & \ell \\ -m_1 & m_1 & m \end{matrix}\right) \right] c_{\bar{\lambda}_2 \lambda_1}(\mathbf{q}_1) \\
& + 0(\mathbf{q}) \tag{D.3}
\end{aligned}$$

For $\ell \neq 0$ the restricted sum in (D.3) is generically non-zero. Therefore, it is for $\ell \neq 0$:

$$\sum_{\lambda''} v^{\alpha}(\mathbf{q}, \lambda | \mathbf{q}_1 \lambda_1; \mathbf{q}_2 \lambda_2; \lambda'') = 0(1) \tag{D.4}$$

For $\lambda = (0,0)$ the Clebsch-Gordon coefficients $C(\ell_1 \ell_2 0; m_1 m_2 0)$ are non-zero for $\ell_1 = \ell_2$ and $m_1 + m_2 = 0$ only. Therefore, both restricted sums in (D.3) do vanish and it remains

$$\begin{aligned}
& \sum_{\lambda''} v^{\alpha}(\mathbf{q}, \lambda | \mathbf{q}_1 \lambda_1; \mathbf{q}_2 \lambda_2; \lambda'') = \\
& = \left[b_{\ell_2 \ell_2 0}^{\alpha}(\mathbf{q}\mathbf{q}_1)C\left(\begin{matrix} \ell_2 & \ell_2 & 0 \\ -m_2 & m_2 & 0 \end{matrix}\right) + (-1)^{\ell_1+\ell_2+m_1+m_2} b_{\ell_1 \ell_1 0}^{\alpha}(-\mathbf{q}\mathbf{q}_1)C\left(\begin{matrix} \ell_1 & \ell_1 & 0 \\ -m_1 & m_1 & 0 \end{matrix}\right) \right] c_{\bar{\lambda}_2 \lambda_1}(\mathbf{q}_1) \\
& \quad + 0(\mathbf{q}) \\
& = \begin{cases} 0(\mathbf{q}) & , \quad \alpha = T \\ 0(1) & , \quad \alpha = R \end{cases} \tag{D.5}
\end{aligned}$$

where (56) and (B.6) has been used.

Appendix E: Result for $c_\ell^m(\mathbf{q})$

The direct correlation function $c_{\ell m; \ell' m'}(\mathbf{q})$ becomes diagonal in the \mathbf{q} -frame and in MSA:

$$c_{\ell m; \ell' m'}(\mathbf{q}, \mathbf{t}) \cong c_\ell^m(\mathbf{q}) \delta_{\ell \ell'} \delta_{m m'} \quad . \quad (\text{E.1})$$

To calculate $c_{\ell m; \ell' m'}(\mathbf{q}, \mathbf{t})$ from (73) it is important to note that we keep $\mathbf{q} \neq 0$ and perform the limit volume $V \rightarrow \infty$ first, and afterwards the limit $\mathbf{q} \rightarrow 0$ 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. (68)). As a result we get:

$$c_0^0(y) = 16\pi^2 d^3 y^{-6} \left\{ \left[24c_3 - 2c_1 y^2 \right] + \right. \quad (\text{E.2})$$

$$\left. + \left[-24c_3 y + (c_0 + 2c_1 + 4c_3) y^3 \right] \sin y + \right.$$

$$\left. + \left[-24c_3 + (2c_1 + 12c_3) y^2 - (c_0 + c_1 + c_3) y^4 \right] \cos y \right\}$$

$$c_1^0(y) = 16\pi^2 d^3 y^{-6} \left\{ \left[8 \left(c_\Delta^{(3)} + 4c_D^{(3)} \right) - \frac{2}{3} \left(c_\Delta^{(1)} + 8c_D^{(1)} \right) y^2 \right] + \right. \quad (\text{E.3})$$

$$\left. + \left[-8 \left(c_\Delta^{(3)} + 4c_D^{(3)} \right) y + \frac{1}{3} \left(c_\Delta^{(0)} + 2c_\Delta^{(1)} + 4c_\Delta^{(3)} + 10c_D^{(1)} + 14c_D^{(3)} - 2 \frac{\beta \mu^2}{d^3} \right) \cdot y^3 \right] \sin y + \right.$$

$$\left. + \left[-8 \left(c_\Delta^{(3)} + 4c_D^{(3)} \right) + \left(\frac{2}{3} c_\Delta^{(1)} + 4c_\Delta^{(3)} + \frac{16}{3} c_D^{(1)} + 16c_D^{(3)} \right) y^2 - \frac{1}{3} \left(c_\Delta^{(0)} + \right. \right.$$

$$\left. c_{\Delta}^{(1)} + c_{\Delta}^{(3)} + 2c_D^{(1)} + 2c_D^{(3)} - 2\frac{\beta\mu^2}{d^3}y^4 \right\} \cos y \Bigg\}$$

and

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

where $y = qd$ is the dimensionless wavenumber and

$$c_{\Delta}^{(v)} = 2\kappa [c_v(2\kappa\varphi) - c_v(-\kappa\varphi)] \quad , \quad v = 0,1,3$$

$$c_D^{(1)} = \frac{1}{4}\kappa [2c_1(2\kappa\varphi) + c_1(-\kappa\varphi)] \quad (\text{E.5})$$

$$c_D^{(3)} = \frac{1}{2}\kappa [2c_3(2\kappa\varphi) + c_3(-\kappa\varphi)]$$