

On the theory of light scattering in molecular liquids

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Abstract. The theory of light scattering for a system of linear molecules with anisotropic polarizabilities is considered. As a starting point for our theory, we express the result of a scattering experiment in VV and VH symmetry as dynamic correlation functions of tensorial densities $\rho_{lm}(q)$ with $l = 0$ and $l = 2$. l, m denote indices of spherical harmonics. To account for all observed hydrodynamic singularities, a generalization of the theory of Schilling and Scheidsteger [1] for these correlation functions is presented, which is capable to describe the light scattering experiments from the liquid regime to the glassy state. As a microscopic theory it fulfills all sum rules contrary to previous *phenomenological* theories. We emphasize the importance of the helicity index m for the microscopic theory by showing, that only the existence of $m = 1$ components lead to the well known Rytov dip in liquids and to the appearance of transversal sound waves in VH symmetry in the deeply supercooled liquid and the glass. Exact expressions for the phenomenological frequency dependent rotation translation coupling coefficients of previous theories are derived.

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1 Introduction

In 1957 Rytov [2] predicted, based on a macroscopic phenomenological theory, that the depolarized light scattering should show a dip at zero frequency. Later in the 60's it was indeed found experimentally [3] that the light scattering of a liquid in VH geometry, where the plane of polarization of the incident light and the scattered light are perpendicular to each other, shows a symmetric doublet at ± 1 GHz, with a minimum at zero frequency. However Rytov's theory only showed to be in superficial agreement with the experiments.

In the following time a number of theoretical attempts have been made to understand the spectra. In general the intensity of the scattered light I^{SI} is proportional to the correlation function of the fluctuations in the components $\alpha_{\text{SI}}(\mathbf{q}, t)$ of the total polarizability tensor and to the incident light I^{I} . Scattering in VH geometry is of particular interest since the direct (VV or HH) contributions are dominated by Brillouin peaks which correspond to propagating sound waves. In an ideal depolarized spectrum the Brillouin lines will be absent and therefore further information of the low frequency dynamics of the system can be obtained.

It is most commonly believed that in molecular liquids, where anisotropic single molecule polarizability fluctuations are the main cause of depolarized spectra, the dip is

caused by the coupling of molecular orientations to some part of the stress tensor. These theories can all be understood in the framework of the Mori-Zwanzig projection technique by using different variables for the projection scheme. Some primary variable is picked which couples *via* a memory kernel to other secondary variables. Until the end of the 70th however the generalized viscosities which occur in the memory kernel were assumed to be time independent.

In 1969 Volterra [4] used the orientations as a primary variable to which the stress tensor couples which he believed to have – due to symmetry reasons – a nonzero matrix element with the total polarizability. Anderson and Pecora proposed in 1971 [5] a theory which used only the symmetric part of the stress tensor as a secondary variable. Keyes and Kivelson in 1972 [6] used the total polarizability as a primary variable and the momentum density as a secondary. Ailawadi *et al.* [7] in 1972 coupled the spin angular momentum density to the asymmetric part of the stress tensor.

At that time it became evident that when reaching towards the supercooled regime additional features occurred *e.g.* additional site peaks or a central peak which could not be explained consistently by any of the above two variable theories. Therefore a number of theories were developed with additional variables (and an additional number of adjustable parameters). Quentrec in 1976 [8] used the whole second rank tensor of the orientations and Chappell *et al.* in 1981 [9] coupled the momentum density and an

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unspecified symmetric tensor to the total polarizability. And also a four variable theory with 7 adjustable parameters was proposed [10]. Wang in 1980 [11] was the first to introduce time dependent generalized viscosities which can account for retardation effects in the memory functions. An approach which got refined and improved later on [12,13]. The authors of [12] and [13] emphasize the importance of retardation – (memory) – effects in the coupling coefficients between the rotational and translational degrees of freedom. Since all the mentioned theories are phenomenological, it is difficult to decide, which one will give the “correct” description of the spectra. As an important result of our theory, which we are going to present, we will show, how the most complex of the mentioned phenomenological theories [13] can be derived microscopically as a special approximation to a more complete set of equations. Thereby microscopic expressions for the phenomenological coupling constants in [13] are presented.

All of the above theories have in common, that they deal with the theory of the experimental technique (light scattering) and the dynamic of the system, which is measured in light scattering, on equal footing. One important deficiency of the early theories, is a too simplistic treatment for the dynamic of the liquid (*e.g.* assuming white noise spectra for the in general frequency dependent generalized viscosities [5]), although the phenomenology for the light scattering part is correct. From a conceptual point of view, a clear distinction between these two topics should be made. The question which quantity is measured, can and should be answered first. In a second, and we would like to stress, *independent* step, a theory for the measured quantity can be formulated. This strategy was already pursued in the generalized hydrodynamic approach of [14], where – without specifying the scattering mechanism – a completely general treatment of the effect of hydrodynamic singularities and the influence of slow structural relaxations on light scattering spectra was achieved, by deriving formally exact expressions for frequency dependent Pockels constants and related Green Kubo relations.

Also in our approach the two mentioned questions are clearly separated. But contrary to [14], we will formulate a theory for a specific scattering mechanism, to get some more insight in the microscopic mechanisms. We will show in Section 5, that the formal structure of the theory is compatible with [14]. First we will derive the quantities, which are measured in an ideal light scattering experiments at linear molecules, where all interaction induced effects can be neglected. Then, we present a set of microscopic equations, which in principal enable us to calculate these quantities for a supercooled liquid close to the glass transition. In a final step we approximate our equations very drastically, keeping only the necessary ingredients for a qualitatively correct description of the light scattering experiments. This step is only for pedagogical reasons, to demonstrate the ability of the theory to reproduce light scattering spectra close to the glass transition.

This paper is organized as follows: In Section 2 we derive the direct contribution to the light scattering spec-

trum of a liquid of linear molecules. It will provide the starting point for the following theoretical considerations.

In Section 3 we present a straight forward generalization of the molecular mode coupling theory [1] for linear molecules, which in addition to the orientational and translational degrees of freedom also describes the coupling to transversal current fluctuations. In Section 4 we formulate a restricted *not* self consistent theory, which still contains all hydrodynamic modes and the most important rotational degrees of freedom. As a further, very drastic approximation, we set up a simple Maxwell theory to demonstrate that all qualitative features, observed in light scattering experiments in supercooled liquids are reproduced already within the restricted theory, by changing only the time scale of the structural relaxation. In Section 5 the relation to other light scattering theories is discussed. The phenomenological equations of [13] are derived within our theory and shown to be a special case of the restricted theory.

2 Light scattering from molecular systems

Following [15] the total polarizability of a molecular liquid can be expressed as a sum of single particle and interaction induced many particle contributions.

$$\begin{aligned} \alpha(r - r')E^{\text{ext}}(r') = & \sum_i \alpha^i \delta(r - r^i) \delta(r' - r^i) E^{\text{int}}(r') \\ & + \sum_{ij} \alpha^{ij} \delta(r - r^i) \delta(r' - r^j) E^{\text{int}}(r') \\ & + \sum_{ijk} \alpha^{ijk} \dots \end{aligned} \quad (1)$$

where the superscript ext denotes the external electric field and int denotes an effective internal field. In this work we are concentrating on the direct contribution for linear molecules only. In a dense liquid other scattering mechanisms like direct and indirect dipole induced dipole scattering mechanism and collision induced scattering mechanisms are also present, in general. For CS₂ *e.g.* it has been argued by Madden and Tildesley [16] that the interaction induced mechanism is the dominant one (although this result has been questioned [17]). For Salol it was found [18,19], that the depolarized light scattering is dominated by scattering at orientational fluctuations. In [18,19] more examples are discussed. A theory for depolarized DID spectra in simple liquids was presented in [20]. A generalization of this work to a hydrodynamic theory of light scattering, which incorporates in principle all possible scattering mechanisms was developed in [14]. Here we want to concentrate on the molecular origin of the depolarized light scattering for a system of linear molecules. A generalization to non linear molecules is straight forward, but to avoid unnecessary complexity, we want to restrict ourselves to linear molecules. The numerical study of water [21,32] has shown, that even the dynamics of this non linear molecule can be reasonably well reproduced by

modeling it as a linear molecule. Only direct contribution of the orientations to the spectra are discussed. All interaction induced contributions are neglected.

For linear molecules the polarization tensor of a single molecule can be written in the form

$$\boldsymbol{\alpha}^{(i)} = a\mathbf{I} + \frac{g}{3}(3\hat{n}^{(i)}\hat{n}^{(i)} - \mathbf{I}). \quad (2)$$

Here $\hat{n}^{(i)}$ is a unit vector in the direction of the principal axis of the molecule i . \mathbf{I} is the identity matrix. The numbers a and g are the mean polarizability and the anisotropy of the polarization respectively.

The collective wave-vector dependent fluctuations of the total polarizability tensor $\boldsymbol{\alpha}(\mathbf{q}, t)$ are defined by

$$\delta\alpha_{\text{SI}}(\mathbf{q}, t) = \sum_{i=1}^N \delta\alpha_{\text{SI}}^{(i)}(t) \exp(i\mathbf{q}\mathbf{r}_i(t)). \quad (3)$$

Here the indices S, I denote the direction of the scattered and incident light, respectively. The fluctuation of the single molecule polarizability $\delta\alpha_{\text{SI}}^{(i)}(t)$ is completely due to rotations of the molecule.

The light scattering intensity is then given by

$$\begin{aligned} I_{\text{SI}}(q, \omega) &\sim FT(\langle \alpha_{\text{SI}}^*(\mathbf{q}, t) \alpha_{\text{SI}}(\mathbf{q}, 0) \rangle) \\ &= \int_{-\infty}^{\infty} dt e^{i\omega t} \\ &\times \langle \sum_{i,j} \alpha_{\text{SI}}^{(i)*}(t) e^{-i\mathbf{q}\mathbf{r}_i(t)} \alpha_{\text{SI}}^{(j)}(0) e^{i\mathbf{q}\mathbf{r}_j(0)} \rangle \end{aligned} \quad (4)$$

where the $\langle \rangle$ brackets denote a thermal expectation value. Usually the convention is used that the xz -plane is the scattering plane and the scattering vector is anti-parallel to the z -axis (see Fig. 1). In this geometry the depolarized scattering in VV and VH geometry, respectively, read:

$$I^{\text{VV}}(q, \omega) = I_{\text{I}} FT(\langle \delta\alpha_{yy}(q, t) \delta\alpha_{yy}(q, 0) \rangle)(\omega) \quad (5)$$

$$\begin{aligned} I^{\text{VH}}(q, \omega) &= I_{\text{I}} FT(\langle \delta\alpha_{yx}^*(q, t) \delta\alpha_{yx}(q, 0) \rangle \sin^2(\Theta/2) \\ &+ \langle \delta\alpha_{yz}^*(q, t) \delta\alpha_{yz}(q, 0) \rangle \cos^2(\Theta/2))(\omega) \end{aligned} \quad (6)$$

where Θ is the scattering angle, $q = |\mathbf{q}|$ and FT denotes the Fourier transform. For linear molecules, the specified scattering frame is equivalent to the so called q -frame, where the z -axis is parallel to the scattering vector \mathbf{q} , since the polarizability tensor is a spherical tensor of rank two, where only $l = 0$ and $l = 2$ components appear (see Appendix C). These are invariant under reflection $\mathbf{q} \rightarrow -\mathbf{q}$. The explicit form of $\boldsymbol{\alpha}$ in the q -frame is derived in Appendix C. With (C.6) we arrive at the result

$$\begin{aligned} I^{\text{VV}}(q, \omega) &\sim a^2 S''_{00}(q, \omega) + g^2 \frac{4\pi}{15} \left(S''_{22}(q, \omega) \right. \\ &\left. + \frac{1}{3} S''_{22}(q, \omega) \right) - ag \frac{4}{3} \sqrt{\frac{\pi}{5}} S''_{20}(q, \omega) \end{aligned} \quad (7)$$

$$\begin{aligned} I^{\text{VH}}(q, \omega) &\sim g^2 \frac{4\pi}{15} (\sin^2(\Theta/2) S''_{22}(q, \omega) \\ &+ \cos^2(\Theta/2) S''_{22}(q, \omega)). \end{aligned} \quad (8)$$

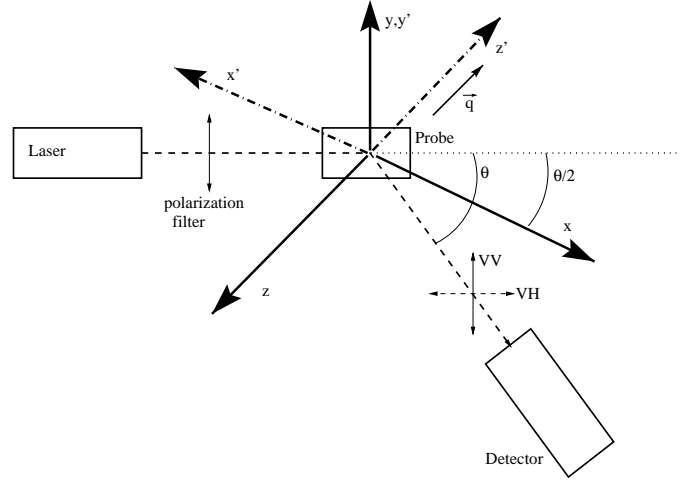


Fig. 1. The possible scattering geometries for a light-scattering experiment. The coordinate system which is denoted with (x, y, z) is the common coordinate system used in light scattering theories. The coordinate system which is denoted with (x', y', z') is the q -frame usually used in theoretical descriptions for the dynamics of liquids where the z -axis points along the q -vector (arrow) which is probed.

In the derivation of equations (7) and (8) we used that in the q -frame, the dynamic structure factors $S_{ll'}^{mm'}(q, t)$ are diagonal with respect to m, m' and that for linear molecules $S_{ll'}^m(q, t) = S_{ll'}^{-m}(q, t)$. The contribution $\sim S''_{20}(q, \omega)$ will be neglected in the following. It is of relative order q compared to $S''_{22}(q, \omega)$ and $S''_{00}(q, \omega)$ in light scattering experiments at liquids for $\omega = cq$ and will only contribute to the intensity of the Brillouin line in glasses.

Similar equations were already derived in [22] for the special case of a diluted gas, where translational and rotational motion can be factorized. In the case of dense liquids, the form equations (7) and (8) have to be used. For a system of linear molecules with only direct but anisotropic scattering mechanism, they provide a complete and exact description of the observed light scattering spectra. Since we are interested in light scattering experiments in supercooled liquids, we are going to present a microscopic theory for the generalized dynamic structure factors $S_{ll'}^m(q, t)$ which contains all observed features of light scattering experiments close to the glass transition. Already from the general form of (7) and (8) some general conclusions can be drawn.

First, due to the scattering angle Θ in the VH geometry a backscattering geometry only observes the $m = 2$ component of the dynamic density correlation function whereas a 90 degrees scattering angle probes a mixture of $m = 1$ and $m = 2$ components. In the following sections we show that the $S''_{22}(q, \omega)$ and $S''_{22}(q, \omega)$ component couple to the longitudinal and transverse sound mode, respectively, while the $S''_{22}(q, \omega)$ component does not couple to any hydrodynamic mode. Therefore it is possible to replace $S''_{22}(q, \omega)$ by its value at $q = 0$, but not the correlators with $m = 0, 1$. The different behavior of the

correlators with different m is due to a dynamic breaking of the rotational invariance on the spatial scale of the light scattering experiments, caused by the existence of hydrodynamic singularities. The phenomenological form for the light scattering spectra used in the literature can be recovered by rewriting equations (7) and (8) in the form

$$I^{VV}(q, \omega) \sim a^2 S''_{00}(q, \omega) + g^2 \frac{4\pi}{15} \left[\frac{4}{3} S''_{22}(q=0, \omega) + \frac{1}{3} \left(S''_{22}(q, \omega) - S''_{22}(q=0, \omega) \right) \right] \quad (9)$$

$$I^{VH}(q, \omega) \sim g^2 \frac{4\pi}{15} \left[S''_{22}(q=0, \omega) + \cos^2(\Theta/2) \times (S''_{22}^1(q, \omega) - S''_{22}(q=0, \omega)) \right]. \quad (10)$$

Here we have used that for $q=0$ due to rotational symmetry all correlation functions with different helicity m but the same l are equal and are therefore replaced with $m=0$. In addition we have neglected the off diagonal contribution $S''_{20}(q, \omega)$. The last two terms in equations (9) and (10) contain hydrodynamic poles and thus are essential for the understanding of light scattering experiments. For theoretical considerations it is more convenient to use equations (7) and (8). Therefore we continue in this work using the representation in spherical harmonics.

Second, the spectra fulfill sum rules. The total intensities $I_{\text{tot}}^{\text{SI}} = \int d\omega I_{\text{tot}}^{\text{SI}}(\omega)$ for $q \rightarrow 0$ are derived from equations (7) and (8)

$$I_{\text{tot}}^{\text{VV}}(q=0, t=0) \sim a^2 S''_{00}(q=0, t=0) + g^2 \frac{4\pi}{15} \frac{4}{3} S''_{22}(q=0, t=0) \quad (11)$$

$$I_{\text{tot}}^{\text{VH}}(q=0, t=0) \sim g^2 \frac{4\pi}{15} S''_{22}(q=0, t=0). \quad (12)$$

Here we used, that the static structure factor $S''_{ll'}^m(q=0, t=0)$ are independent of m and diagonal in l, l' . Therefore the anisotropic part of $I_{\text{tot}}^{\text{VV}}$ is exactly equal to $\frac{4}{3} I_{\text{tot}}^{\text{VH}}$.

Third, we note the well established fact, that the often used procedure to obtain the isotropic scattering contribution (*e.g.* in [23], see also [22]) by simply subtracting $\frac{4}{3} I^{\text{VH}}$ from $I^{\text{VV}}(\omega)$ is in general not exact, since there are big qualitative differences between the correlation functions $S''_{22}^m(q, \omega)$ for different m , due to the coupling of translational and rotational motion. In Appendix 7B of [22] the mentioned relation between $I^{\text{VV}}(\omega)$ and $I^{\text{VH}}(\omega)$ could be derived by explicitly assuming, that rotational and translational motion are independent. But it is clear, that this cannot hold in dense liquids, where the rotation of a molecule can easily cause the build up of local stress *via* interaction with its neighbors. This stress can then be released by a center of mass motion of neighboring molecules. Instead of obtaining only the isotropic contribution the mentioned subtraction method will yield the

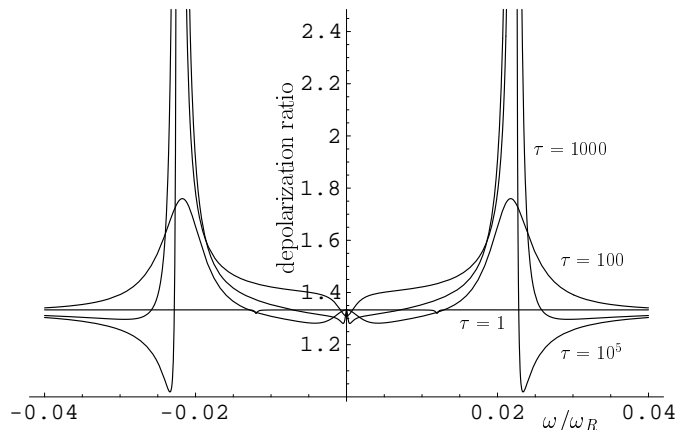


Fig. 2. The depolarization ratio for backscattering geometry $D(q, \omega) = \left((S''_{22}(q, \omega) + 1/3 S''_{22}(q=0, \omega)) / S''_{22}(q, \omega) \right)$ for some arbitrary chosen parameters. In units of the rotational frequency $\omega^R \equiv 1$, the other parameters where chosen as $c_{\parallel} = 0.6$, $G_S = 1$, $\nu_R = 5$, $K_1 = 1$, $K_R = 1$, $K_{\text{IR}} = K_{\text{SR}} = 1/2$. The values of the α -relaxation time τ were set identical for all components with $\tau = \tau_1 = \tau_R = \tau_{\text{SR}} = \tau_{\text{IR}} = \tau_S \in \{1, 0.01, 0.001, 10^{-5}\}$.

following expression

$$I^{\text{VV}}(q, \omega) - \frac{4}{3} I^{\text{VH}}(q, \omega) \sim a^2 S''_{00}(q, \omega) + g^2 \frac{4\pi}{45} \times \left[S''_{22}(q, \omega) - S''_{22}(q=0, \omega) - 4 \cos^2(\Theta/2) \times (S''_{22}^1(q, \omega) - S''_{22}(q=0, \omega)) \right]. \quad (13)$$

Equation (13) shows, that even in back scattering geometry deviations from the purely isotropic scattering are to be expected. To demonstrate this point in more detail, we plot in Figure 2 the value of the depolarization ratio in backscattering geometry ($\Theta = \pi$) for a simple model which we derive from our equations (see Sect. 4). To further demonstrate the result of equation (13) we have (using the same model discussed in Sect. 4) further plotted the quantity $(S''_{22}(q, \omega) - S''_{22}(q=0, \omega)) / S''_{00}(q, \omega)$. This is done on a linear scale in Figure 14 and on a logarithmic frequency scale in Figure 15. It can be clearly seen that deep in the liquid phase ($\tau = 1$) it is practically zero whereas strong deviations occur especially around the Brillouin lines when supercooling the liquid. From equations (9) and (10) it follows that the depolarization ratio in general is given by

$$\frac{S''_{22}(q, \omega) + \frac{1}{3} S''_{22}(q=0, \omega)}{\sin^2(\Theta/2) S''_{22}(q, \omega) + \cos^2(\Theta/2) S''_{22}^1(q, \omega)} = \frac{4}{3} + \frac{1}{3} \times \frac{S''_{22}(q, \omega) - S''_{22}(q=0, \omega)}{S''_{22}(q=0, \omega) + \cos^2(\Theta/2) (S''_{22}^1(q, \omega) - S''_{22}(q=0, \omega))}. \quad (14)$$

In backscattering geometry ($\Theta = \pi$) it is nearly constant in the liquid and given by $4/3$ whereas strong deviations

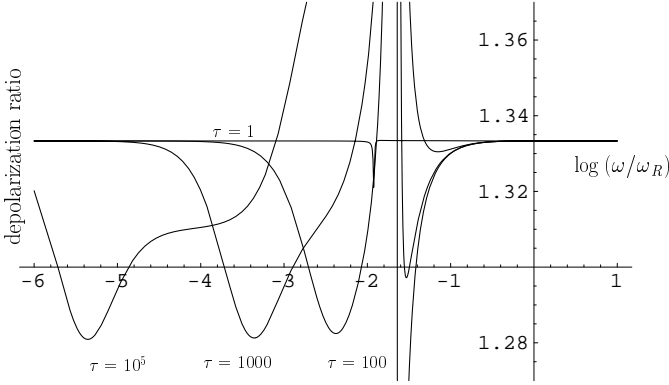


Fig. 3. The depolarization ratio for the same parameters as in Figure 2 on a logarithmic frequency scale.

occur around the Brillouin line when supercooling the liquid. These deviations are expected to be even bigger when the experiment is performed not in backscattering geometry since in this case the $m = 1$ component which couples to the transverse phonon will also contribute. Figure 3 shows the depolarization ratio on a logarithmic frequency scale. The deviations of the depolarization ratio from $4/3$ are also seen in the experiment and are discussed in [18]. Therefore we have proven that the quantity $I_{VV} - 4/3 I_{VH}$ is *not* proportional to $S_{00}^{0''}(q, \omega)$, especially not around the Brillouin lines. We are aware that this is a severe difficulty in interpreting light-scattering experiments and want to point out that in the low frequency regime it is usually not applied anyway, since I_{VH} becomes very weak.

3 The equation of motion of linear molecules

After having an exact expression for the scattered intensities (see Eqs. (7) and (8)), we turn in this section to the second and independent step in order to arrive at a microscopic understanding of light scattering spectra. This second step is the discussion of a microscopic theory of a molecular liquid. The mode coupling theory of the glass transition has by now proven to be a very successful microscopic theory to describe the dynamics of supercooled liquids close to the glass transition (for a recent review see *e.g.* [24,25]). In its early version [26] only simple liquids consisting of spherical molecules were described microscopically. Due to its successful application also to experiments and simulations at arbitrary molecules it became necessary to develop generalizations to molecular liquids [1, 21, 27–29]. Also aspects of these generalized theories were successfully tested in simulations [30–32]. The main quantity, which is studied in [1] is the coherent dynamic structure factor $S_{ll'}^m(\mathbf{q}, t)$ for linear molecules. The theory describes on a microscopic basis the coupling of translational and orientational degrees of freedom, but does not take into account the coupling to transversal currents. In [21] the theory for the dynamic structure factor $S_{ll';nn'}^{mm'}(\mathbf{q}, t)$ of arbitrary rigid molecules was derived.

This theory deals also with the transversal currents, but is at present difficult to reduce to linear molecules. Since all theories of light scattering agree in the importance of transversal current fluctuations, it will be necessary to formulate a theory for linear molecules, which also contains coupling to transversal currents. Fortunately this theory is a straight forward generalization of the theory in [1]. We do not take into account energy fluctuations in our derivation, which were necessary to describe the Rayleigh peak *i.e.* the influence of heat diffusion on the light scattering spectrum. We do not expect important changes for the discussion of the light scattering spectrum, by neglecting the influence of heat fluctuations. For a discussion of the interplay of structural relaxation and heat diffusion see [33,14].

The MMCT is derived within a Mori-Zwanzig projection operator formalism for tensorial densities $\rho_{lm}(\mathbf{q}, t)$

$$\rho_{lm}(\mathbf{q}, t) = \sqrt{4\pi} i^l \sum_{i=1}^N Y_{lm}(\Omega_i(t)) e^{i\mathbf{q}\mathbf{r}_i(t)} \quad (15)$$

with $Y_{lm}(\Omega)$ being the spherical harmonics and tensorial currents $\{j^\alpha\}_{lm}(\mathbf{q}, t)$. The index $\alpha = T, R$ denote translational currents and rotational currents, respectively. For linear molecules it is not necessary to use the orientational current as a vectorial quantity. The only quantity which will appear in the theory is

$$\{j_0^R\}_{lm}(\mathbf{q}, t) = \frac{\sqrt{4\pi}}{\sqrt{l(l+1)}} i^l \sum_{i=1}^N (\boldsymbol{\omega}\mathbf{L}) Y_{lm}(\Omega_i(t)) e^{i\mathbf{q}\mathbf{r}_i(t)}. \quad (16)$$

Here \mathbf{L} is the angular momentum operator and $\boldsymbol{\omega}$ is the angular velocity. $\{j_0^R\}_{lm}(\mathbf{q}, t)$ with $m \in \{-l, -l+1, \dots, l-1, l\}$ are the components of an irreducible spherical tensor of rank l .

To be able to describe light scattering spectra we will need all components of the translational current fluctuations $\{j_\mu^T\}_{lm}(\mathbf{q}, t)$, $\mu \in \{-1, 0, 1\}$, not only its projection along \mathbf{q} as in [1]. Here we used spherical components μ instead of Cartesian components $\{x, y, z\}$

$$\{j_\mu^T\}_{lm}(\mathbf{q}, t) = i^l \sqrt{4\pi} \sum_{i=1}^N v_\mu Y_{lm}(\Omega_i(t)) e^{i\mathbf{q}\mathbf{r}_i(t)} \quad (17)$$

with

$$\begin{aligned} \{j_{\pm 1}^T\}_{lm}(\mathbf{q}, t) &= \frac{-1}{\sqrt{2}} (\pm \{j_x^T\}_{lm}(\mathbf{q}, t) + i \{j_y^T\}_{lm}(\mathbf{q}, t)) \\ \{j_0^T\}_{lm}(\mathbf{q}, t) &= \{j_z^T\}_{lm}(\mathbf{q}, t). \end{aligned} \quad (18)$$

The translational currents $\{j_\mu^T\}_{lm}(\mathbf{q}, t)$ can be written as a sum of components of an irreducible spherical tensor $\{j_{\hat{l}\hat{m}}^T\}_{l\hat{m}}^{\text{irr}}(\mathbf{q}, t)$

$$\{j_\mu^T\}_{lm}(\mathbf{q}, t) = \sum_{\hat{l}, \hat{m}} C(1\hat{l}; \mu m \hat{m}) \{j_{\hat{l}\hat{m}}^T\}_{l\hat{m}}^{\text{irr}}(\mathbf{q}, t) \quad (19)$$

with $|l-1| \leq \hat{l} \leq l+1$ and $\hat{m} = m + \mu$, due to the properties of the Clebsch-Gordan coefficients $C(l_1 l_2 l; m_1 m_2 m)$. As an important special case we note, that the transversal center of mass currents $(j_{\pm 1}^T)_{00}(\mathbf{q}, t)$ have irreducible spherical components $\{j_{\pm 1}^T\}_{1\pm 1}^{\text{irr}}(\mathbf{q}, t)$.

The currents and the densities fulfill a continuity equation

$$\frac{d}{dt} \rho_{lm}(q, t) = \sum_{\mu, \alpha} i(-1)^\mu q_{-\mu}^\alpha (l) \{j_\mu^\alpha\}_{lm}(q, t) \quad (20)$$

with

$$q_\mu^\alpha(l) = \begin{cases} q_\mu & \text{for } \alpha = \text{T} \\ \sqrt{l(l+1)} & \text{for } \alpha = \text{R} \end{cases} \quad (21)$$

With the help of Mori-Zwanzig projection operator techniques [1, 34], it is possible to derive a formally exact set of equations for the correlation functions $S_{ll'}^{mm'}(\mathbf{q}, t)$ of the tensorial densities $\rho_{lm}(\mathbf{q}, t)$. For simplicity we write the equation in the q -frame *i.e.* ($\mathbf{q} = q(0, 0, 1)$). For a short ranged potential every correlation function $(A_{lm}(q, t)|B_{l'm'}(q)) = \langle A_{lm}(q, t)^* B_{l'm'}(q) \rangle$ of two components $A_{lm}(q, t)$, $B_{l'm'}(q)$ of irreducible spherical tensors fulfill the relations

$$\begin{aligned} (A_{lm}(q, t)|B_{l'm'}(q)) &= \delta_{mm'} (A_{lm}(q, t)|B_{l'm}(q)) \quad (22) \\ (A_{lm}(q, t)|B_{l'm}(q)) &\sim q^{|l-l'|} \text{ for } q \rightarrow 0. \end{aligned}$$

The first line of (22) is just due to the fact that under a rotation around the z -axis, $(A_{lm}(q, t)|B_{l'm'}(q))$ will transform into $e^{i(m'-m)\phi} (A_{lm}(q, t)|B_{l'm'}(q))$. Since the correlation function has to be invariant under this operation, the relation (22) follows. The second line is a consequence of global rotational invariance of the system of linear molecules. In addition, the correlation function $(A_{lm}(q, t)|B_{l'm}(q))$ is independent of m for $q = 0$, if there are no long range correlations, which destroy the global rotational invariance. For correlation functions which behave regular at $q = 0$ *i.e.* which do not contain any hydrodynamic poles, we are allowed to replace them for small q by their value at $q = 0$ plus corrections. If there are hydrodynamic poles, the differences between different m can be crucial *e.g.* we will see, that the dynamic correlation function $S_{22}^m(q, z)$ contains for $m = 1$ even at small values of q couplings to transversal current fluctuations, where the one for $m = 2$ behaves regular at $q \rightarrow 0$.

The dynamic correlation function $S_{ll'}^{mm'}(q, t)$ is a real quantity [1]. Since we will discuss in the following part of the paper also current-current correlation functions we use the notation $S_{ll'}^m(q, t) \equiv (\phi_{\pm\rho\rho}^m)_{ll'}^{mm}(q, t)$ The equation

for $\phi_{\pm\rho\rho}^m(q, t)$ is therefore

$$\begin{aligned} \frac{\partial}{\partial t} \phi_{\pm\rho\rho}^m(q, t) &= -i \underline{\mathbf{q}} \phi_{\pm j_\rho}^m(q, t) \equiv -i \sum_{\alpha} q_{\pm\alpha}^\alpha \phi_{\pm j_\alpha^\alpha}^m(q, t) \\ \frac{\partial}{\partial t} \phi_{\pm j_\rho}^m(q, t) &= -i \underline{\Gamma}_{\pm j_\rho}(q) \phi_{\pm\rho\rho}^m(q, t) \\ &\quad - \int_0^t dt' \underline{M}_{\pm j_\rho}^m(q, t-t') \phi_{\pm j_\rho}^m(q, t) \\ \frac{\partial}{\partial t} \phi_{\pm j_\rho j'}^m(q, t) &= -i \underline{\mathbf{q}} \phi_{\pm j_\rho j'}^m(q, t) \equiv -i \sum_{\alpha} q_{\pm\alpha}^\alpha \phi_{\pm j_\alpha^\alpha j'}^m(q, t) \\ \frac{\partial}{\partial t} \phi_{\pm j_\rho j'}^m(q, t) &= -i \underline{\Gamma}_{\pm j_\rho j'}(q) \phi_{\pm\rho j'}^m(q, t) \\ &\quad - \int_0^t dt' \underline{M}_{\pm j_\rho j'}^m(q, t-t') \phi_{\pm j_\rho j'}^m(q, t) \quad (23) \end{aligned}$$

where we use the short-hand notation $\mathbf{j} = \{j_\mu^\alpha\}_{lm}$, $\mathbf{j}' = \{j_{\mu'}^{\alpha'}\}_{l'm'}$ and $\underline{\mathbf{q}} = \delta_{ll'}(-1)^\mu q_{-\mu}^\alpha(l)$, $\phi_{\pm j_\mu^\alpha}^m(q, t) = \delta_{m', m+\mu} \times (\{j_\mu^\alpha\}_{lm}(q, t) | \rho_{lm'}(q, 0))$, $\phi_{\pm\rho j_\mu^\alpha}^m(q, t) = \phi_{\pm j_\mu^\alpha}^m(q, t)$ and $\phi_{\pm j_\mu^\alpha j_{\mu'}^{\alpha'}}^m(q, t) = \delta_{m+m', m'+m'} (\{j_\mu^\alpha\}_{lm}(q, t) | \{j_{\mu'}^{\alpha'}\}_{l'm'}(q, 0))$ are the current-density, density-current and current-current correlation functions, respectively. The matrix $\underline{\Gamma}_{\pm j_\rho}(q) = \delta_{\mu, 0} q_{\pm\alpha}^\alpha \frac{k_B T}{\Theta_\alpha} (\mathbf{S}^{-1}(q, m))$ is determined by the static molecular correlators. Θ_T and Θ_R are the mass and inertia, respectively. The products $q_{\pm\alpha}^\alpha \underline{\Gamma}_{\pm j_\alpha^\alpha}^m(q)$ and $q_{\pm\alpha}^\alpha \underline{\Gamma}_{\pm j_\alpha^\alpha j_\beta^\beta}^m(q)$ are the matrix of rotational and translational microscopic frequencies, respectively. The memory matrix $\underline{M}(q; t) = \underline{M}_{\mu\mu'}^{\alpha\alpha'} = \{M_{\mu\mu'}^{\alpha\alpha'}\}_{m, m'}^{l, l'}(q; t) = (Q\mathcal{L}(\{j_\mu^\alpha(q)\}_{lm} | R'(t) | Q\mathcal{L}(\{j_{\mu'}^{\alpha'}(q)\}_{l'm'})) \frac{\Theta_{\alpha'}}{k_B T}$ is a frequency dependent damping matrix, \mathcal{L} is the Liouville operator, Q is the projection operator perpendicular to the density- and current fluctuations (see Eqs. (15, 16) and (17)). $R'(t)$ is a reduced time translation operator $R'(t) = Q e^{iQ\mathcal{L}Q t}$ [34]. The memory matrix is *not* diagonal in m and m' , contrary to the one appearing in [1]. This is due to the fact, that the currents for $\mu \neq 0$ are not components of an irreducible spherical tensor. Instead, due to (19) and (22) the relation $m' = m + \mu$ has to be fulfilled:

$$\{M_{\mu, \mu'}^{\alpha, \alpha'}\}_{m, m'}^{l, l'}(q; t) = \delta_{m+\mu, m'+\mu'} \{M_{\mu, \mu'}^{\alpha, \alpha'}\}_{m, m'}^{l, l'}(q; t). \quad (24)$$

Without the memory matrix equation, (23) would describe a system of coupled undamped harmonic “modes”, where the modes are in this case correlation functions of tensorial densities. The physical origin of the memory matrix is the damping of these oscillatory modes due to interaction between them including translation rotation couplings, caused by the anharmonicities of the microscopic interaction potentials. Of special importance will be the induction of a stress $\mathcal{L}\{j_1^T\}_{00}(q, t)/q$ by the force $\mathcal{L}\{j_0^R\}_{21}(q, t)$ caused by the rotation of the molecules. This mechanism is responsible for the existence of hydrodynamic singularities in auto correlation functions of non hydrodynamic fluctuations.

$$\begin{pmatrix} z\underline{I} & -\underline{\mathbf{q}} \\ -\underline{\Gamma}_{\underline{\mathbf{j}}\rho} & z\underline{I} + \underline{\underline{M}}_{\underline{\mathbf{j}}\underline{\mathbf{j}}} \end{pmatrix} = \begin{pmatrix} z\delta_{ll'}\delta_{mm'} & -\delta_{ll'}\delta_{mm'}(-1)^\mu q_{-\mu}^\alpha(l) \\ -\delta_{\mu,0}\frac{k_{\text{B}}T}{\Theta_\alpha}q_0^\alpha\delta_{mm'}(\mathbf{S}^{-1})_{ll'}^m(q) & z\delta_{ll'}\delta_{mm'} + \{M_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'}(q, z) \end{pmatrix}. \quad (33)$$

3.1 Molecular mode coupling theory

Within the MMCT, the memory functions are written as a sum of bare Markovian damping terms plus mode coupling terms. The mode coupling terms have the form of self consistent statically renormalized one loop approximations.

$$M_{\mu\mu'}^{\alpha,\alpha'}(q; t-t') = i\nu_{\mu\mu'}^{\alpha,\alpha'}(q)\delta(t-t') + \frac{k_{\text{B}}T}{\Theta_\alpha}m_{\mu\mu'}^{\alpha,\alpha'}(q; t-t'). \quad (25)$$

The derivation of the mode coupling approximations is analogous to the one in [1]. For the memory functions with $\mu = \mu' = 0$ the final result is identical to [1]. For general μ, μ' , it can be written

$$\begin{aligned} \{m_{\mu,\mu'}^{\alpha,\alpha'}\}_{l,l'}^{m,m'}(q; t) &\approx \frac{1}{2N} \left(\frac{\rho_0}{4\pi}\right)^2 \sum_{\mathbf{q}_1\mathbf{q}_2} \sum_{m_1m_2} \sum_{l_1l_2} \sum_{l'_1l'_2} \\ &\times \{V_{\mu,\mu'}^{\alpha\alpha'}\}_{l,l',l_1,l'_1,l_2,l'_2}^{m,m',m_1,m_2}(q, q_1, q_2) S_{l_1l'_1}^{m_1}(q_1, t) S_{l_2l'_2}^{m_2}(q_2, t), \end{aligned} \quad (26)$$

with

$$\begin{aligned} \{V_{\mu,\mu'}^{\alpha\alpha'}\}_{l,l',l_1,l'_1,l_2,l'_2}^{m,m',m_1,m_2}(q, q_1, q_2) &:= \\ \{v_\mu^\alpha\}_{l,l_1,l_2}^{m,m_1,m_2}(q, q_1, q_2) \{v_{\mu'}^{\alpha'}\}_{l',l'_1,l'_2}^{m',m'_1,m'_2}(q, q_1, q_2)^*, \end{aligned} \quad (27)$$

$$\begin{aligned} \{v_\mu^\alpha\}_{l,l_1,l_2}^{m,m_1,m_2}(q, q_1, q_2) &:= \\ \sum_{l_3} \{u_\mu^\alpha\}_{l,l_3,l_2}^{m,m_1,m_2}(q, q_1, q_2) c_{l_3,l_1}^{m_1}(q_1) + (-1)^m (1 \longleftrightarrow 2) \end{aligned} \quad (28)$$

where $c_{l,l'}^m(q)$ is the direct correlation function and

$$\begin{aligned} \{u_\mu^\alpha\}_{l,l_1,l_2}^{m,m_1,m_2}(q, q_1, q_2) &:= \\ i^{l_1+l_2-l} \left[\frac{(2l_1+1)(2l_2+1)}{(2l+1)} \right]^{\frac{1}{2}} \frac{1}{2} [1 + (-1)^{l_1+l_2+l}] \\ &\times \sum_{m'_1m'_2} (-1)^{m'_2} d_{m'_1m_1}^{l_1}(\Theta_{q_1}) d_{m'_2m_2}^{l_2}(\Theta_{q_2}) C(l_1l_2l; m'_1m'_2m) \\ &\times \begin{cases} q_1(\mu) C(l_1l_2l; 000) & ; \alpha = \text{T} \\ \sqrt{l_1(l_1+1)} C(l_1l_2l; 101) & ; \alpha = \text{R} \end{cases}. \end{aligned} \quad (29)$$

Here the functions $q_1(\mu)$ are given by

$$\begin{aligned} q_1(\mu) &= q_1 \sqrt{\frac{4\pi}{3}} \left(\mu Y_{1\mu}(\Theta_{q_1}, \Phi_{q_1}) \right. \\ &\left. + (1 - |\mu|) Y_{10}(\Theta_{q_1}, \Phi_{q_1}) \right). \end{aligned} \quad (30)$$

The functions $d_{m'm}^l(\Theta)$ are related to Wigner's rotation matrices (we follow the notation of Gray and Gubbins [35]). For given Euler angles Φ, Θ, χ they are defined as [35]

$$D_{mm'}^l(\Phi, \Theta, \chi) = e^{-im\Phi} d_{mm'}^l(\Theta) e^{-im'\chi} \quad (31)$$

$q_i, \Theta_{q_i}, \Phi_{q_i}$ are the standard spherical coordinates of \mathbf{q}_i with respect to \mathbf{q} . The prime at the first summation in equation (26) restricts $\mathbf{q}_1, \mathbf{q}_2$ such, that $\mathbf{q}_1 + \mathbf{q}_2 = \mathbf{q}$ in order to fulfill momentum conservation. Equations (23, 26, 27) form a set of self consistent equations for the generalized dynamic structure factors $S_{ll'}^m(q, t)$ of linear molecules. They are slightly more general than the equations in [1] by including the coupling to transverse current fluctuations *via* a rotation-translation coupling. It is to be expected that this coupling will affect the results for the glass transition temperatures and the non ergodicity parameters studied in [1,30] only quantitatively but not qualitatively [36]. The dynamics, instead, can be changed qualitatively in certain wave vector-ranges. Especially for small wave vectors the hydrodynamic pole in the transverse current fluctuations can have large effects on the density relaxation spectrum. We will demonstrate explicitly in the next chapter, that the coupling to transverse current fluctuations is necessary to reproduce the appearance of transverse sound modes in Brillouin scattering spectrum of linear molecules, within the framework of MMCT.

To calculate the light scattering spectra it is most convenient to perform a Laplace transform of equation (23). With $LT(f(t))(z) = i \int_0^\infty e^{izt} f(t)$, with $\text{Im}(z) > 0$, we obtain the following matrix equation

$$\begin{pmatrix} z\underline{I} & -\underline{\mathbf{q}} \\ -\underline{\Gamma}_{\underline{\mathbf{j}}\rho} & z\underline{I} + \underline{\underline{M}}_{\underline{\mathbf{j}}\underline{\mathbf{j}}} \end{pmatrix} \begin{pmatrix} \underline{\underline{\phi}}_{\rho\rho}(z) & \underline{\underline{\phi}}_{\rho\mathbf{j}}(z) \\ \underline{\underline{\phi}}_{\mathbf{j}\rho}(z) & \underline{\underline{\phi}}_{\mathbf{j}\mathbf{j}}(z) \end{pmatrix} = - \begin{pmatrix} \underline{\underline{\phi}}_{\rho\rho}^0 & \underline{\underline{\phi}}_{\rho\mathbf{j}}^0 \\ \underline{\underline{\phi}}_{\mathbf{j}\rho}^0 & \underline{\underline{\phi}}_{\mathbf{j}\mathbf{j}}^0 \end{pmatrix}. \quad (32)$$

Here we have chosen a simplified notation. In the q -frame the first matrix in equation (32) would be explicitly:

see equation (33) above.

The matrix of static correlators on the right hand side of equation (32) is

$$\begin{pmatrix} \underline{\underline{\phi}}_{\rho\rho}^0 & \underline{\underline{\phi}}_{\rho\mathbf{j}}^0 \\ \underline{\underline{\phi}}_{\mathbf{j}\rho}^0 & \underline{\underline{\phi}}_{\mathbf{j}\mathbf{j}}^0 \end{pmatrix} = \begin{pmatrix} \delta_{mm'} S_{ll'}^m(q) & 0 \\ 0 & \delta_{\mu\mu'} \delta_{\alpha\alpha'} \delta_{mm'} \delta_{ll'} \frac{k_{\text{B}}T}{\Theta_\alpha} \end{pmatrix}. \quad (34)$$

It is obvious from equations (32) and (33) that the sum rules (11) and (12) are automatically fulfilled, if the approximations for the memory functions obey the very weak requirement, that $\lim_{z \rightarrow \infty + i\epsilon} \frac{\{M_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'}}{z} = 0$, where

ϵ is an arbitrary positive number. Since memory functions are regular for $t = 0$ in most physical cases, they even vanish as $1/z$ for $z \rightarrow \infty$. This property is especially fulfilled for the selfconsistent MMCT and also for the primitive theory used in Section 4.

4 Glassy dynamics and hydrodynamic modes

Light scattering usually measures at small wave vectors q . Therefore the correct treatment of hydrodynamic modes becomes crucial for explaining light scattering experiments. To obtain the generalized density correlation $S_{ll'}^m(q, t)$ for small wave-vectors, it would be necessary to solve the self consistent set of equations (23, 26, 27) for *all* wave-vectors and *all* l, m , since all degrees of freedom are coupled *via* mode coupling integrals. To study the light scattering problem, we first want to restrict the discussion to the fluctuations, which are most relevant for the understanding of light scattering experiments. These are the density fluctuation $\rho_{lm}(q, t)$ for $(l, m) = (0, 0)$ and $2, m$ their respective current fluctuations $\{j_0^T\}_{00}(q, t)$, $\{j_0^R\}_{2m}(q, t)$, which are directly measured in light scattering experiments (*i.e.* $l = 0, 2$ and $m = 0, 1, 2$) and the current fluctuations $\{j_\mu^T\}_{00}(q, t)$, which are slow, since the total currents $\{j_\mu^T\}_{00}(q = 0, t)$ are conserved. Here we have also neglected the current fluctuations $\{j_0^T\}_{2m}(q, t)$. Their contribution will be of higher order in q , as can be seen by comparing the translational and rotational current contribution in the first line of (23) together with (21). Additional simplification occur in the limit $q \rightarrow 0$, due to relation (22) for correlation functions of spherical tensors in a rotationally invariant system.

1. The static correlation function is $S_{ll'}^m(q = 0) = \delta_{ll'} S_l \equiv S_{ll'}^m(q = 0)$, independent of m .
2. The component of the matrix $\underline{\Gamma}_{\underline{j}\rho}$ of equation (32) with $l = l' = m = \mu = 0$ and $\alpha = T$ reduces to $\frac{k_B T}{m S_{00}(q)} q = c_{\parallel}^2 q$. Here c_{\parallel} is the longitudinal isothermal sound velocity in the liquid.
3. The component of the matrix $\underline{\Gamma}_{\underline{j}\rho}$ of equation (32) with $l = l' = 2$, $\mu = 0$ and $\alpha = R$ reduces to $\frac{k_B T}{\Theta S_2(q)} \sqrt{6} = \frac{\omega_B^2}{\sqrt{6}}$, where ω_B is a classical frequency, related to the rotation of the quadrupoles.
4. The memory matrix $\{M_{00}^{TT}\}_{00}^{00}(i0)$ has to reduce to $i\eta q^2$, where $\eta = \eta_B + \frac{4}{3}\eta_S$ is the longitudinal viscosity of the liquid. The transversal memory function is for $q \rightarrow 0, z \rightarrow i0$ given by $\{M_{11}^{TT}\}_{00}^{00}(i0) = iq^2\eta_S$, where η_S is the shear viscosity. The q^2 dependence of the translational memory functions $\{m_{\mu\mu'}^{TT}\}_{00}^{00}$ are due to momentum conservation. The parameter $\{K_{\mu\mu'}^{TT}\}_{00}^{00}$

and $\{\tau_{\mu\mu'}^{TT}\}_{00}^{00}$ in (35) are identical to the longitudinal modulus K_1 and the longitudinal α -relaxation time τ_l for $\mu = \mu' = 0$ and the shear modulus G_S and the transverse α -relaxation time τ_S for $\mu = \mu' = 1$, respectively. With this choice the Maxwell relations $\eta_l = \eta_l^0 + K_1\tau_B$ and $\eta_S = \eta_S^0 + G_S\tau_S$, where η_l^0, η_S^0 are the contribution from the Markovian part of the memory matrix, are fulfilled in the liquid.

Due to the local nature of the cage effect, which is responsible for the slowing down of structural relaxations, it is strictly speaking not possible to study self-consistently the hydrodynamic limit, without the knowledge of relaxations on local length scales $r \propto r_0$, where r_0 is on the scale of intermolecular distances. But since the memory functions $\mathbf{m}_{\mu,\mu'}^{\alpha,\alpha'}(q, t)$ do not contain any hydrodynamic pole by construction, they are non trivial only due to the glass transition dynamics, which in turn is independent of the hydrodynamic fluctuations at short wavelength. It is *e.g.* theoretically understood [37] and verified in simulations [38], that systems with qualitatively different hydrodynamic behavior exhibit the same glassy dynamics. To obtain the qualitative behavior of equations (23, 26, 27), it is therefore sufficient to replace the mode coupling part of the memory function matrix by its leading wave-vector behavior multiplied with a function, which is able to describe glassy dynamics. Although the memory functions are free of hydrodynamic singularities, they exhibit the full frequency dependence of glassy dynamics (“fast” and “slow” β -relaxations, α -relaxation plus additional complications as *e.g.* contributions from Bose peak phenomena [39, 40]). For reproducing all details of light scattering spectra, which are directly related to glassy dynamics, two approaches are possible. Either an ansatz has to be found, which is compatible with all the mentioned phenomena, or the full set of microscopic equations, derived in Section 3, had to be solved numerically, to account at least for β - and α -relaxation, (see *e.g.* [41]). But before this very difficult problem can be treated, it is necessary to demonstrate, that the structure of the equations derived in Section 3 can account for all the hydrodynamic poles and their interplay with the most basic phenomena of structural relaxations *i.e.* the α -relaxation. To achieve that, it is sufficient to use an α -relaxation ansatz for the memory function. To make the analysis as simple and explicit as possible, we choose simple exponentials (Maxwell theory) for the non vanishing memory functions, multiplied with their leading wave vector dependence, q^n , $n \in \{0, 1, 2\}$

$$\{m_{\mu,\mu'}^{\alpha,\alpha'}\}_{l,l'}^{m,m'}(q, z) = -\frac{q^n \{K_{\mu,\mu'}^{\alpha,\alpha'}\}_{l,l'}^{m,m'}(q) \{\tau_{\mu,\mu'}^{\alpha,\alpha'}\}_{l,l'}^{m,m'}}{z \{\tau_{\mu,\mu'}^{\alpha,\alpha'}\}_{l,l'}^{m,m'} + i} . \quad (35)$$

The small wave vector behavior of the memory functions (35) can be derived from (22) and (19) and the conservation laws for total momentum in every spatial direction for $l = 0$ or $l' = 0$. The relaxation times $\{\tau_{\mu,\mu'}^{\alpha,\alpha'}\}_{l,l'}^{m,m'}$ are taken at $q = 0$. The projection operator formalism guarantees,

that this value is nonzero, since the memory functions do not contain hydrodynamic poles. The Markovian part of the memory functions is in the following neglected, if it would vanish at wave vector $q = 0$. There are two severe consequences of this approximation together with the α -relaxation ansatzes for the memory functions. First the sound poles in the glass do not show any damping, instead of a damping proportional to q^2 . Second, a fit with the Maxwell ansatz or any other ansatz, which only describes the α -relaxation, would lead to an artificial time scale separation for the α -relaxation times of the different memory functions (see *e.g.* the discussion in [13]). The source of both errors, is the neglect of “fast” β -relaxation phenomena, which also contribute to the memory functions.

The task is now to show, that the predicted spectra are consistent with sum rules and the qualitative behavior of light scattering experiments, which already follow very generally from a purely generalized hydrodynamic analysis [14] and that the interplay of rotational and translational motions lead to the qualitatively correct renormalizations of the hydrodynamic poles, when entering the glassy regime.

If we order our basic variables in the form $\rho_{00}, \rho_{2m}, \{j_0^R\}_{2m}, \{j_1^T\}_{00}$, the frequency independent matrices appearing in equation (32) are

$$\underline{\underline{\mathbf{q}}} = \begin{pmatrix} q & & & 0 \\ & \sqrt{6} & & 0 \\ & & \sqrt{6} & 0 \\ & & & \sqrt{6} \end{pmatrix}$$

$$\underline{\underline{\Gamma}}_{j\rho} = \begin{pmatrix} c_{\parallel}^2 q & & & & \\ & \omega_R^2/\sqrt{6} & & & \\ & & \omega_R^2/\sqrt{6} & & \\ & & & \omega_R^2/\sqrt{6} & \\ 0 & 0 & 0 & 0 & \omega_R^2/\sqrt{6} \\ & & & & 0 \end{pmatrix}. \quad (36)$$

The slow part of the memory matrix is given by

$$z\underline{\underline{I}} + \underline{\underline{m}}_{\mathbf{jj}} = \begin{pmatrix} z - \frac{q^2 K_{1T}}{z\tau_{1+1}} & -\frac{qK_{1R}\tau_{1R}}{z\tau_{1R+1}} & & & \\ -\frac{qK_{1R}\tau_{1R}}{z\tau_{1R+1}} r & z - \frac{K_{1R}\tau_{1R}}{z\tau_{1R+1}} & & & \\ & & z - \frac{K_{R}\tau_{R}}{z\tau_{R+1}} & & -\frac{qK_{SR}\tau_{SR}}{z\tau_{SR+1}} r \\ & & & z - \frac{K_{R}\tau_{R}}{z\tau_{R+1}} & \\ & & & & z - \frac{q^2 G_S \tau_S}{z\tau_{S+1}} \end{pmatrix} \quad (37)$$

where $r = \frac{\Theta_T}{\Theta_R}$.

The leading wave-vector dependence for $q \rightarrow 0$ of the matrix elements is derived from conservation laws and equation (22). All the matrix elements, which are left empty are exactly zero due to m, m' selection rules (see Eq. (22)). For the appearance of transversal sound modes in the light scattering spectra and the explanation of the Rytov Dip it is crucial that $K_{SR} \neq 0$, which quantifies the memory matrix-element between the transversal current for $l = 0$ and the rotational current j_{2m}^R for $m = 1$. The four parameters K_1, K_R, K_{1R} and K_{SR} have to be such

that the memory matrix remains positive definite for all frequencies. For $z = 0$ the relation

$$K_1 K_R \tau_{1R} - K_{1R}^2 \tau_{1R}^2 r > 0$$

$$\text{and } K_R G_S \tau_S \tau_R - K_{SR}^2 \tau_{SR}^2 r > 0 \quad (38)$$

follow and the diagonal elements K_1, K_R and G_S have to be positive. We also note that the exact relations

$$G_S K_R \geq K_{SR}^2 r \quad (39)$$

$$K_1 K_R \geq K_{1R}^2 r \quad (40)$$

can be derived from the Cauchy relations

$$\{m_{11}^{TT}\}_{00}''(\omega) \{m_{00}^{RR}\}_{22}''(\omega) \geq \{m_{10}^{TR}\}_{02}''(\omega)^2 r \quad (41)$$

$$\{m_{00}^{TT}\}_{00}''(\omega) \{m_{00}^{RR}\}_{22}''(\omega) \geq \{m_{00}^{TR}\}_{02}''(\omega)^2 r \quad (42)$$

by considering the low and high frequency limits of equations (41) and (42).

4.1 Hydrodynamic poles

Before we discuss the numerical solution of equation (32), it is useful to investigate its hydrodynamic poles. The only conserved quantities are (besides the total energy) the center of mass density and the total momentum in every spatial direction. They are the cause of the hydrodynamic poles (*i.e.* poles which show dispersion laws $z \propto q^n$, with $n = 1, 2$) in the respective auto correlation functions $\langle \Phi_{\rho\rho} \rangle_{00}^0$ and $\{(\Phi_{\mathbf{jj}})_{\mu\mu}^{TT}\}_{00}^{00}$. But due to the dynamic coupling of the rotational degrees of freedom and the translational degrees of freedom, which appear naturally in the memory matrix, also the correlation functions of non hydrodynamic variables do exhibit hydrodynamic poles. To study this phenomena, we invert the matrix in equation (32), use the ansatz $z = pq^n$, $n \in \{0, 1, 2\}$ and expand the denominator in powers of q . For $n = 0$ this gives poles of non-hydrodynamic nature (rotational modes with a frequency p), for $n = 1$ propagating modes (transverse or longitudinal phonon modes) are described with p being the sound velocity and for $n = 2$ a diffusive mode with a transport coefficient (in our case generalized viscosity) $-p/i$ is obtained.

Let's first study the transversal current fluctuations. In a *simple* liquid the transversal current correlator $\{(\Phi_{\mathbf{jj}})_{11}^{TT}\}_{00}^{00}(z)$ exhibits a viscous pole at $z = -iG_S \tau_S q^2$. This is also the case for the liquids of linear molecules, studied in this paper. But in addition, due to the translation rotation coupling, also the auto correlation functions of densities $\rho_{lm}(q, t)$ or currents $\{j_0^T\}_{lm}$ with $l = 2, m = 1$ do exhibit the transversal hydrodynamic poles. The reason for that is, that the tensor $\{j_1^T\}_{00}$ has irreducible spherical components with $l = 2, m = 1$, and thus is able to couple dynamically to the specified tensors *via* the memory functions with $m = 1$. There is also a non-hydrodynamic singularity related to the rotational motion of the molecules. If we restrict the correlators to their poles (neglecting the glassy dynamics), the poles

of the $(\Phi_{\rho\rho})_{22}^1(z)$, $\{(\Phi_{\mathbf{jj}})_{00}^{\text{RR}}\}_{22}^{11}(z)$, $\{(\Phi_{\mathbf{jj}})_{11}^{\text{TT}}\}_{00}^{00}(z)$ components are given by:

$$(z^2 + i(K_{\text{R}}\tau_{\text{R}} + \nu_{\text{R}})z - \omega_{\text{R}}^2) (z + iG_{\text{S}}\tau_{\text{S}}q^2) = 0. \quad (43)$$

The two poles couple into the dynamic correlators with different amplitudes. The coupling of the second pole into the $l = 2, m = 1$ rotational component causes the Rytov dip. As an example we therefore give the the term in lowest order of q of the strength of the transverse sound mode coupling into the $(\Phi_{\rho\rho})_{22}^1(z)$ component. In the vicinity of the Rytov dip this component can be expressed as:

$$(\Phi_{\rho\rho})_{22}^1(z) = \frac{-K_{\text{SR}}^2\tau_{\text{SR}}^2q^2}{\omega_{\text{R}}^2} \left(\frac{-6S_2r}{z + iG_{\text{S}}\tau_{\text{S}}q^2} \right). \quad (44)$$

Therefore the strength of the Rytov dip is proportional to q^2 times the matrix element which couples the transverse current to the $m = 1$ rotational motion and vanishes if the rotational frequency ω_{R} goes to infinity.

As soon as $z\tau_{\text{S}} \gg 1$, the diffusive pole will turn into a propagating transversal sound mode. In simple liquids this pole will be at $z = \pm\sqrt{G_{\text{S}}}q$. Whereas in *molecular* liquids the transversal sound velocity is renormalized by contributions of the rotational degrees of freedom. The pole structure of the specified correlators $(\Phi_{\rho\rho})_{22}^1(z)$, $\{(\Phi_{\mathbf{jj}})_{00}^{\text{RR}}\}_{22}^{11}(z)$, $\{(\Phi_{\mathbf{jj}})_{11}^{\text{TT}}\}_{00}^{00}(z)$ is in the supercooled regime given by:

$$(z^2 + i\nu_{\text{R}}z - \omega_{\text{R}}^2 - K_{\text{R}}) \left(z^2 - (G_{\text{S}} - \frac{K_{\text{SR}}^2r}{(K_{\text{R}} + \omega_{\text{R}}^2)})q^2 \right) = 0. \quad (45)$$

I.e. the transversal sound pole is given by

$$z = \pm\sqrt{G_{\text{S}} - \frac{K_{\text{SR}}^2r}{(K_{\text{R}} + \omega_{\text{R}}^2)}} q := \pm c_{\perp}q. \quad (46)$$

The transverse sound velocity is shifted to smaller frequencies compared to what is expected in a simple liquid. This trend was already noted in [13]. Note, that due to the positivity of ω_{R}^2 and the exact relation (39), the transversal sound velocity is always well defined. *I.e.* by treating the rotation translation coupling explicitly, we are able to describe the contribution of the rotational motion to the transversal sound velocity c_{\perp} . The microscopic rotational translational coupling is the cause of the appearance of hydrodynamic poles in correlation functions of non hydrodynamic (*i.e.* for $q \rightarrow 0$ non conserved) variables and of a renormalization of the transversal sound velocity. Analogous behavior is found for center of mass and longitudinal current fluctuations. The amplitude of the transverse sound pole in lowest order of q which occurs in the $(\Phi_{\rho\rho})_{22}^1(z)$ component can be derived. It is in the vicinity of the transverse phonon mode given by:

$$(\Phi_{\rho\rho})_{22}^1(z) = \left(\frac{K_{\text{R}}^2(G_{\text{S}}(K_{\text{R}} + \omega_{\text{R}}^2))}{(K_{\text{R}} + \omega_{\text{R}}^2)(K_{\text{SR}}^2(\omega_{\text{R}}^2 - K_{\text{R}})r + G_{\text{S}}K_{\text{R}}(K_{\text{R}} + \omega_{\text{R}}^2))} \right) \times \frac{-6S_2}{z \pm \sqrt{G_{\text{S}} - \frac{K_{\text{SR}}^2r}{(K_{\text{R}} + \omega_{\text{R}}^2)}} q}. \quad (47)$$

Therefore the transverse phonon mode can only be observed as long as the rotation couples *via* K_{R} to the structural relaxation.

In the fluid ($\tau_1 c_{\parallel} q \ll 1$) the longitudinal components with $l = 0, m = 0$ and the rotational components with $l = 2, m = 0$ contain two types of modes. First the $l = 2$ rotational mode and second the longitudinal phonon mode. The poles of $(\Phi_{\rho\rho})_{00}^0(z)$, $(\Phi_{\rho\rho})_{22}^0(z)$, $\{(\Phi_{\mathbf{jj}})_{00}^{\text{TT}}\}_{00}^{00}(z)$, $\{(\Phi_{\mathbf{jj}})_{00}^{\text{RR}}\}_{22}^{00}(z)$ are given by:

$$(z^2 + i(K_{\text{R}}\tau_{\text{R}} + \nu_{\text{R}})z - \omega_{\text{R}}^2) (z^2 - c_{\parallel}^2q^2 + iK_1\tau_1zq^2) = 0. \quad (48)$$

The first pole gives the damped rotation of the molecule, whereas the second term describes the usual longitudinal sound modes in the liquid at $z_{\pm} = \pm c_{\parallel}q$ with the damping $K_1\tau_1q^2/2$. This expression is valid as long as $K_1\tau_1q^2 \ll \tau_1c_{\parallel}q \ll 1$. The amplitude of the longitudinal phonon mode in $(\Phi_{\rho\rho})_{22}^0(z)$ is proportional to q^2 , where it is of order q^0 in $(\Phi_{\rho\rho})_{00}^0(z)$. Its contribution to the sound pole in the I^{VV} -spectrum in the liquid can therefore be neglected.

In the solid ($\tau_1 c_{\parallel} q \gg 1$), the sound pole will be shifted to higher frequencies and, as an artifact of the Maxwell theory, the damping vanishes. An inclusion of β relaxation phenomena will cure this unphysical behavior. We obtain as poles of the $(\Phi_{\rho\rho})_{00}^0(z)$, $(\Phi_{\rho\rho})_{22}^0(z)$, $\{(\Phi_{\mathbf{jj}})_{00}^{\text{TT}}\}_{00}^{00}(z)$, $\{(\Phi_{\mathbf{jj}})_{00}^{\text{RR}}\}_{22}^{00}(z)$ components the solution of:

$$(z^2 + i\nu_{\text{R}}z - \omega_{\text{R}}^2 - K_{\text{R}}) \times \left(z^2 - (c_{\parallel}^2 + K_1 - \frac{K_{\text{IR}}^2r}{(K_{\text{R}} + \omega_{\text{R}}^2)})q^2 \right) = 0 \quad (49)$$

i.e. the longitudinal sound velocity c_{∞} is, as the transversal sound velocity, modified by rotational degrees of freedom

$$c_{\infty}^2 = c_{\parallel}^2 + K_1 - \frac{K_{\text{IR}}^2r}{(K_{\text{R}} + \omega_{\text{R}}^2)}. \quad (50)$$

Due to the positivity of ω_{R}^2 and the exact relation (40) the sound velocity is always shifted to higher values in the glass, but the shift is reduced compared to what would be expected in a simple liquid. In analogy to the transverse mode we can give the low q expansion for the amplitude of the longitudinal sound pole in the $(\Phi_{\rho\rho})_{22}^0(z)$. In the vicinity of the longitudinal phonon frequency this component is given by:

$$(\Phi_{\rho\rho})_{22}^0(z) = \left(\frac{K_{\text{R}}}{K_{\text{R}} + \omega_{\text{R}}^2} \right) \frac{-6S_2}{z \mp \sqrt{c_{\parallel}^2 + K_1 - \frac{K_{\text{IR}}^2r}{(K_{\text{R}} + \omega_{\text{R}}^2)}}}. \quad (51)$$

Therefore a longitudinal phonon in the $(\Phi_{\rho\rho})_{22}^0(z)$ component is always observable in the supercooled liquid as long as the rotational motion couples *via* the matrix element K_{R} to the structural relaxation.

4.2 A solution of the equation of motion

We have now solved the equation of motion for some chosen but fixed parameters. Close to the glass transition it is only the scale of the α -relaxation time, which is changing considerably. If the time temperature superposition principle (TTS) is fulfilled exactly all relaxation times $\{\tau_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'}$ can be written as $\{\hat{\tau}_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'} f(T)$. The function $f(T)$ is the same for all relaxation times and is a quickly changing function of temperature. In the idealized mode coupling theory it would be $(|T - T_c|/T_c)^{-\gamma}$. Often used fit formulas are the Vogel-Fulcher function $f(T) = A \exp(-B/(T - T_0))$ or as a special case the Arrhenius law ($T_0 = 0$). The prefactors $\{\hat{\tau}_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'}$ are constant, but in general different for different combinations of $\mu, \mu', \alpha, \alpha', l, l', m, m'$. Very often the TTS is violated at lower temperatures. In this case also the $\{\hat{\tau}_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'}$ vary slowly with temperature.

Since we are in this paper only interested in qualitative aspects of the solution, all α -relaxation times were taken equal *i.e.* $\{\hat{\tau}_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'} = 1$. The function $f(T)$ is called τ in the following. In this way we demonstrate how we can explain the complete viscosity range from the highly viscous liquid towards the glass by just varying a single parameter, τ .

In the Figures 2–13 we have chosen the following parameters: The frequency scale for the rotational frequency was set to unity $\omega^R = 1$. In these units the other parameters were chosen as $c_{\parallel} = 0.6$, $G_S = 1$, $\nu_R = 5$, $K_1 = 1$, $K_R = 1$, $K_{IR} = K_{SR} = 1/2$, $r = 1$. The external momentum q selected by the scattering experiment is set to $q = 0.02$. For $z\tau \ll 1$ the scattering experiment probes an amorphous solid whereas for $z\tau \gg 1$ it probes a liquid. In all figures the frequency z was chosen to be slightly imaginary: $z = \omega + i \times 10^{-4}$.

In Figure 4 we have plotted from a solution of equation (32) the imaginary part of the center of mass correlator $S_{00}^0(q, z)$ which according to equation (7) forms the main part of the polarized light scattering intensity $I^{VV}(\omega)$. For $\tau = 1 \ll (c_{\parallel}q)^{-1}$ the Brillouin line, caused by a longitudinal sound wave, is at $c_{\parallel}q = 0.012$. The damping is proportional to q^2 (see Eq. (48)). For $\tau = 100 \approx (c_{\parallel}q)^{-1}$ a broad central peak occurs together with a strong damping of the phonon modes. This is a well known phenomena which was already explained by Mountain [42] for the Brillouin spectrum. The same mechanism applies here. If we calculate the hydrodynamic sound pole with the condition $\omega\tau = 1$ the equation for the sound pole is

$$\omega^2 + i\omega\nu q^2 + i\frac{K_1}{2}q^2 - (c_{\parallel}^2 + \frac{K_1}{2})q^2 = 0. \quad (52)$$

This equation can be solved with the ansatz $\omega = c_{\infty}q + i\Gamma q + O(q^2)$ *i.e.* the damping is of order $q \gg q^2$ instead of order q^2 . This effect is even stronger in real glass-formers, where the α -relaxation is better described by a stretched exponential behavior instead of a single exponential. We can estimate, that for frequencies in the high frequency wing of the α -relaxation, where the von Schweidler law applies for the memory-functions ($m(z) \propto (-iz)^{-b}$), the

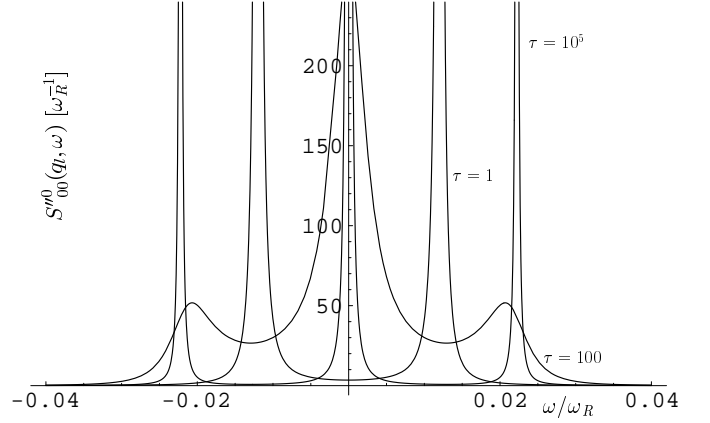


Fig. 4. Solution of equation (32) for the dynamical structure factor $S''_{00}(q, \omega)$. The parameters were set as for Figure 2.

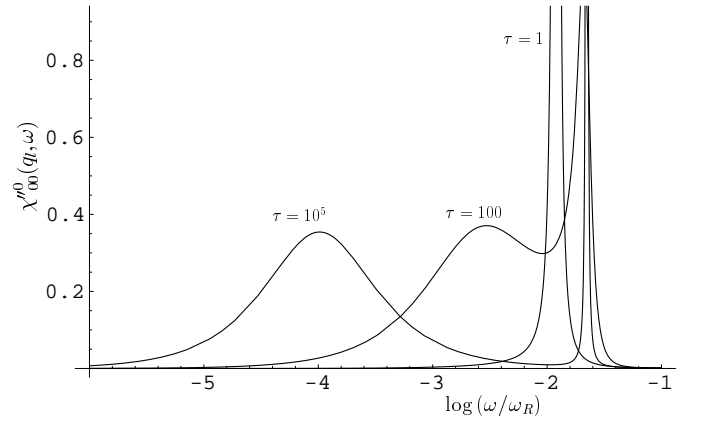


Fig. 5. The susceptibility spectrum $\chi''_{00}(q, \omega) = \omega S''_{00}(q, \omega)$ for the same parameters as in Figure 2 on a logarithmic frequency scale.

pole becomes a cut at $\omega = \pm(\hat{c}_{\infty} + i\Gamma)q^{1-\frac{b}{2}}$. If we include β -relaxation like phenomena with $\omega m''(\omega) \sim \omega^a$, we obtain in the frequency range, where this fractal behavior holds, two strongly damped propagating modes at $\omega = \pm c_{\infty}q + i\Gamma q^{1+a}$. Since the fractal behavior is experimentally observed in depolarized spectra even below T_g , where the α relaxation is far below the experimental frequency range (see *e.g.* [43]), it could account for the anomalous strong damping of the Brillouin line in the sub T_g regime [43]. In this context it is important to note, that the actual physical reason for the appearance of a fractal part of the susceptibility spectrum is not relevant for the described mathematical mechanism of producing strong damping of phonon modes. The β -relaxation phenomenon close to the critical temperature of mode coupling theory is as good a candidate as the still not yet understood fractal behaviour below T_g [43–45]. For $\tau = 10^5 \gg (c_{\parallel}q)^{-1}$ the light scattering probes a solid with a well defined, now renormalized, phonon mode with a renormalized sound velocity which is given by equation (50). As discussed above, the speed of sound in the glass is always bigger than the speed of sound of the liquid.

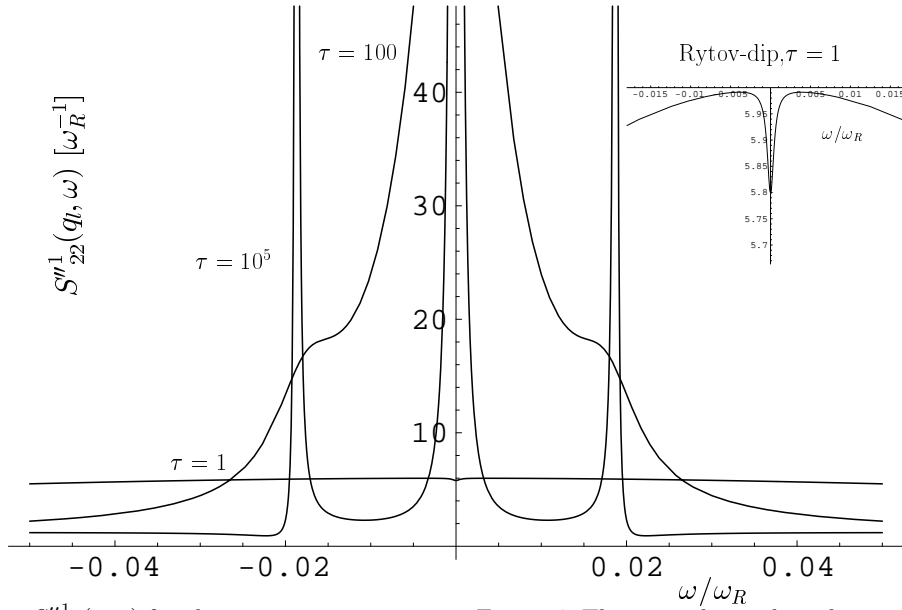


Fig. 6. The spectrum $S''^1_{22}(q, \omega)$ for the same parameters as in Figure 4. The inset shows the value around zero frequency for $\alpha = 1$ to show the Rytov dip.

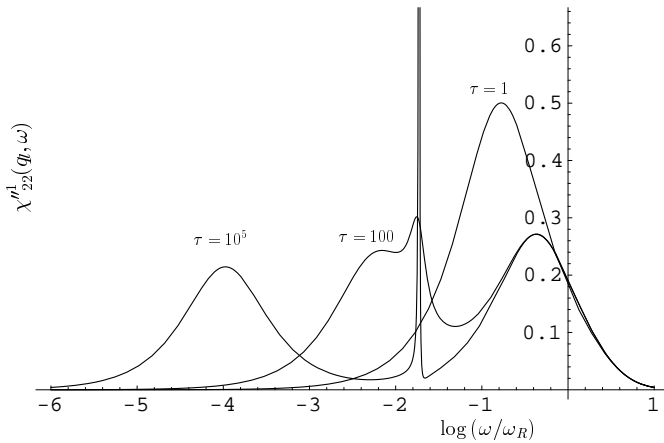


Fig. 7. The susceptibility spectrum $\chi''^1_{22}(q, \omega) = \omega S''^1_{22}(q, \omega)$ on a logarithmic frequency scale. The occurrence of the transverse sound wave can be clearly seen in the supercooled regime.

The next Figure 6 shows the spectral function of $S^1_{22}(q, z)$, which gives the only contribution in forward scattering direction and zero contribution in backscattering geometry for the depolarized geometry due to the $\cos^2(\Theta/2)$ factor (see Eq.(8)). The $S^1_{22}(q, z)$ component is strongly influenced by the coupling of transverse currents to the $m = 1$ rotational current.

$$(\hat{Q}\mathcal{L}\{j_0^R\}_{21}(q)|\frac{-1}{z - \hat{Q}\mathcal{L}\hat{Q}}|\hat{Q}\mathcal{L}\{j_{\pm 1}^T\}_{00}(q)) \approx \frac{qK_{SR}\tau}{z\tau + i}. \quad (53)$$

Deep in the liquid for $\tau = 1 \ll (c_{\parallel}q)^{-1}$ the purely diffusive transverse currents cause the Rytov dip at zero frequencies. This is shown in the inset of Figure 6. When supercooling the liquid the Rytov dip disappears and a broad central peak shows up for $\tau = 100 \approx (c_{\parallel}q)^{-1}$ which

develops a shoulder at the frequency of shear waves. When further supercooling the liquid for $\tau = 10^5 \gg (c_{\parallel}q)^{-1}$ the propagating transversal phonon modes of the solid at $\pm c_{\perp}q$ shows up (see Eq. (46)).

A further contribution to the spectrum of depolarized light scattering according to equation (8) is the $m = 2$ component. Due to the factor $\sin^2(\Theta/2)$ it is the only contribution in backscattering geometry. Since it does not couple to any hydrodynamic mode, it has the simple form

$$S''^2_{22}(\omega) = S^m_{22}(q = 0) \times \frac{6\omega_R^2 \left(\frac{K_R\tau_R}{(\omega\tau)^2 + 1} + \nu_R \right)}{\left(\omega^2 - \omega_R^2 - \frac{\omega^2\tau K_R\tau_R}{(\omega\tau)^2 + 1} \right)^2 + \omega^2 \left(\nu_R + \frac{K_R\tau_R}{(\omega\tau)^2 + 1} \right)^2}. \quad (54)$$

The spectral function of $S^2_{22}(q, z)$ in Figure 8 shows for $\tau = 1 \ll (c_{\kappa}q)^{-1}$ no structure for low energies (far below the rotation spectra). It has no Rytov dip since there is no matrix element which couples shear waves to the $m = 2$ rotational currents. The absence of a Rytov dip is shown explicitly in the inset of Figure 8. When supercooling the liquid a broad central peak shows up for $\tau = 100 \approx (c_{\kappa}q)^{-1}$ which narrows in the solid for $\tau = 10^5 \gg (c_{\kappa}q)^{-1}$. In our units the height of the peak is always $K_R\tau + \nu_R$ and the width is of order $1/\tau$. The absence of transverse modes in backscattering geometry is clearly seen in experiments (see *e.g.* [47] or earlier [48] where light scattering in backscattering geometry was applied to the molecular glass former salol). In other scattering geometries the VH-spectrum exhibits ideally only the transverse phonon (for $\omega\tau_S \gg 1$). We want to point out that there are two qualitatively different mechanism which lead to the observation of a phonon line in a depolarized light scattering geometry.

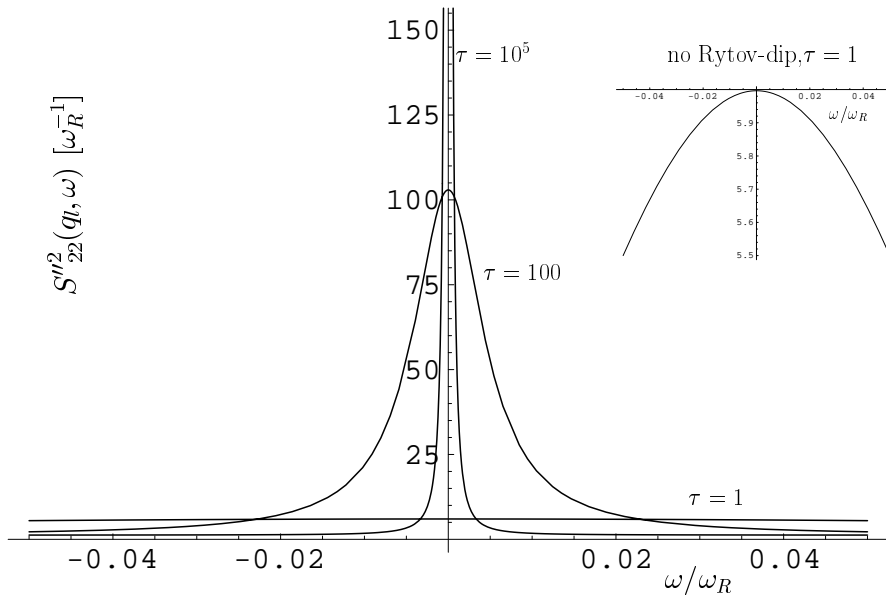


Fig. 8. The spectrum $S''_{22}(q, \omega)$ for the same parameters as in Figure 4. The inset shows the value around zero frequency for $\alpha = 1$ to show the absence of the Rytov dip.

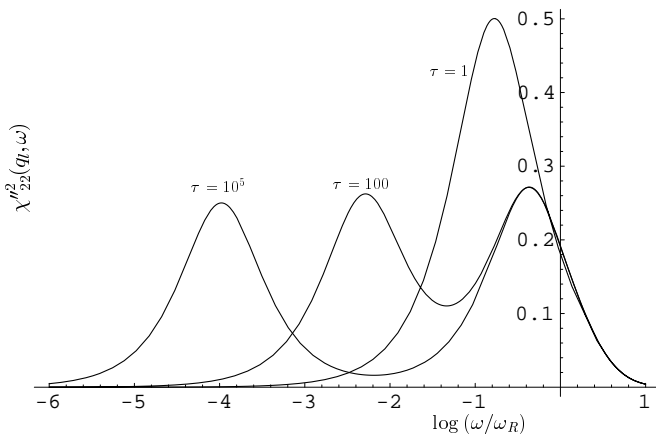


Fig. 9. The susceptibility spectrum $\chi''_{22}(q, \omega) = \omega S''_{22}(q, \omega)$. As in Figure 4 on a logarithmic frequency scale.

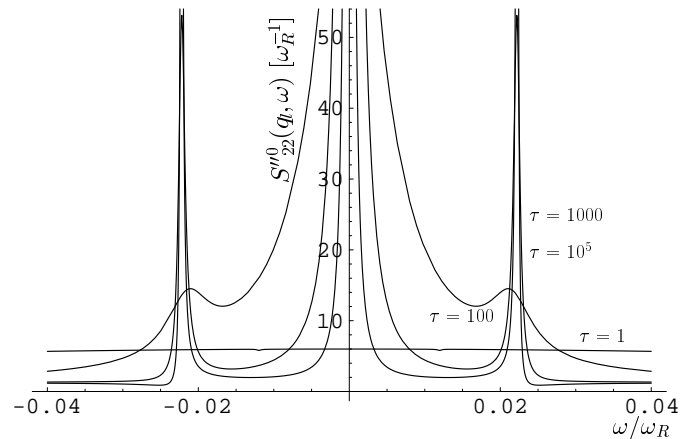


Fig. 10. The spectrum $S''^0_{22}(q, \omega)$ for the same parameters as in Figure 4. The longitudinal phonon couples into this component and becomes observable when the light scattering experiment starts to probe a solid.

The first one is leakage of the longitudinal phonon mode due to an imperfect polarization filter and should not be present in an ideal depolarized geometry. The second one at a lower frequency is a direct transverse phonon which couples to the $S^1_{22}(q, \omega)$ component.

A further contribution which we have plotted is the $S^0_{22}(q, \omega)$ component. It enters according to equation (7) into the intensity for the polarized light scattering geometry. There is a non zero matrix element which couples the longitudinal phonon mode to the $m = 0$ rotational mode which we approximate from equation (32) as

$$\langle \{j_0^T\}_{00}(q) \mathcal{L} \hat{Q} (\hat{Q}(z - \mathcal{L}) \hat{Q})^{-1} \hat{Q} \mathcal{L} \{j_0^R\}_{20}(q) \rangle \approx -\frac{q K_{\text{IR}} \tau}{z\tau + i}. \quad (55)$$

Therefore the longitudinal phonon mode shows up in the $m = 0$ component when the liquid is supercooled. This is shown in Figure 10. For $\tau = 1$ no coupling to the longi-

tudinal phonon mode can be observed. This can easily be understood. The coupling term (55) reduces to $iK_{\text{IR}}\tau q$ for $c_{\parallel}q\tau \ll 1$ at the position of the phonon mode $\omega = c_{\parallel}q$. Since the coupling term to the phonon mode will appear in second order perturbation theory in q , the phonon mode is multiplied with a factor $(K_{\text{IR}}\tau q)^2$ *i.e.* the maximum height of the phonon contribution in the spectrum S''^0_{22} will be of order $K_{\text{IR}}^2\tau/K_1$, which is equal 1, in the units we are using in Figure 10. For $c_{\parallel}q\tau \gg 1$ the coupling term (55) is K_1q/ω *i.e.* at $\omega = c_{\parallel}q$, the coupling constant is of order 1 and the height of the phonon mode is again of order $K_{\text{IR}}^2\tau/K_1 \gg 1$. The phonon mode can be detected as soon as $c_{\parallel}q\tau \sim 1$. In our units this happens for $\tau \sim 50$. In Figure 10 a broad shoulder can be seen for $\tau = 100$, which turns into a clearly defined phonon mode ($\tau = 10^3, \tau = 10^5$).

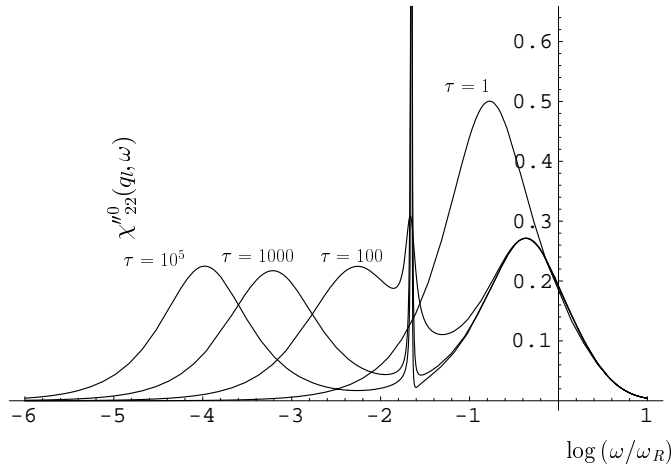


Fig. 11. The susceptibility spectrum $\chi''_{22}(q, \omega) = \omega S''_{22}(q, \omega)$. As in Figure 10 on a logarithmic frequency scale.

The $S''_{00}(q, \omega)$, $S''_{22}(q, \omega)$ and $S''_{22}(q, \omega)$ sum up according to equation (7) to give the total polarized light-scattering intensity. This is plotted in Figure 12 where we have plotted a fictitious VV-spectrum under the additional assumption that the squared isotropic part of the polarizability is ten times as big as the anisotropic one ($a^2 = 10g^2$). Note that the orientational correlator $S''_{22}(q, \omega)$ and the translational center of mass component $S''_{00}(q, \omega)$ are of completely different origin even though a mixing of the poles occurs in the supercooled regime. This is best seen in the liquid regime where the microscopic frequency of the orientation is a rotational motion whereas the microscopic frequency of the center of mass component is given by the longitudinal phonon mode. It is experimentally impossible to extract $S''_{00}(q, \omega)$ out of a measured spectrum except for the case of vanishing anisotropy.

4.3 Susceptibility spectra

In order to make the influence of structural relaxations more transparent, we have plotted on a logarithmic frequency scale the spectral functions of the susceptibilities

$$\chi'''_{ll'}(q, \omega) = \omega S'''_{ll'}(q, \omega) \quad (56)$$

which correspond to the quantities plotted in Figures 4, 6, 8, 10 and 12. Figure 5 shows the spectrum $\chi''_{00}(q, \omega)$. The central peak of Figure 4 turns into an α -peak which upon supercooling the glass transition moves out of the microscopic frequency which is given by the longitudinal phonon mode. We want to stress again that due to our particular simple choice of the memory function (Maxwell theory) the α -peak shown in Figures 5, 7, 9, 11, 13 does not have the correct stretched form known for glassy systems and there is no true β relaxation regime. If the molecular system has no anisotropy (in Eq. (7) $g = 0$) this contribution to light scattering is the only direct one. The area under

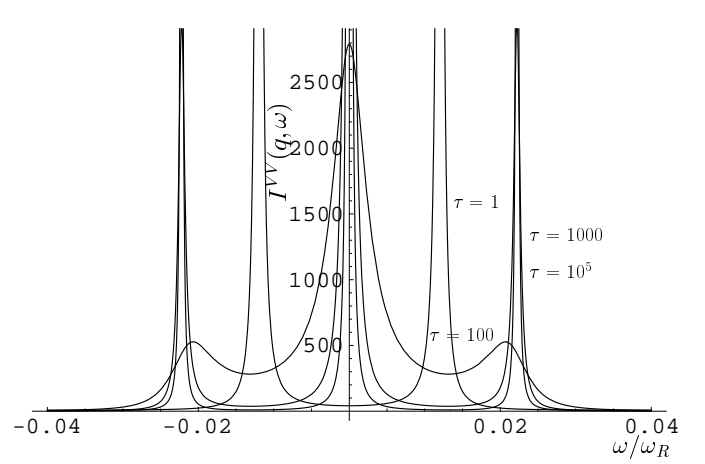


Fig. 12. The VV spectrum for the same parameters as in Figure 4. The square of the isotropic part of the polarizability was assumed to be 10 times as big as the isotropic one $a^2 = 10g^2$. $I^{VV}(q, \omega) \sim a^2 S''_{00}(q, \omega) + \frac{4\pi}{15} g^2 \left(S''_{22}(q, \omega) + \frac{1}{3} S''_{22}(q, \omega) \right)$.

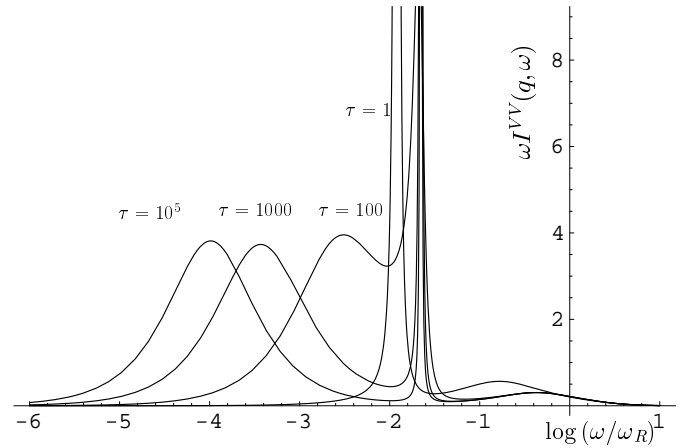


Fig. 13. The susceptibility spectrum $\omega I^{VV}(q, \omega)$ on a logarithmic frequency scale.

the α -peak I_α on a logarithmic frequency scale, which is also the area under the Mountain peak [42] on a linear frequency scale and the overall intensity I_{tot} are in this case related to the non-ergodicity parameter (Edwards-Anderson parameter) $f_{00}^0(q, \omega) = I_\alpha / I_{\text{tot}}$ for the center of mass component.

Figure 7 shows the spectral function of $\chi_{22}^1(q, z)$. The microscopic is given by the rotational $l = 2$ mode roughly at ω_R . When the liquid is supercooled towards the glass transition the shear wave shows up when the α -relaxation moves over the frequency range range for transverse phonons at $\omega = c_\perp q$. As expected the $m = 2$ component $\chi''_{22}(q, \omega)$ in Figure 9 only shows the broad rotational mode and the α -relaxation since there

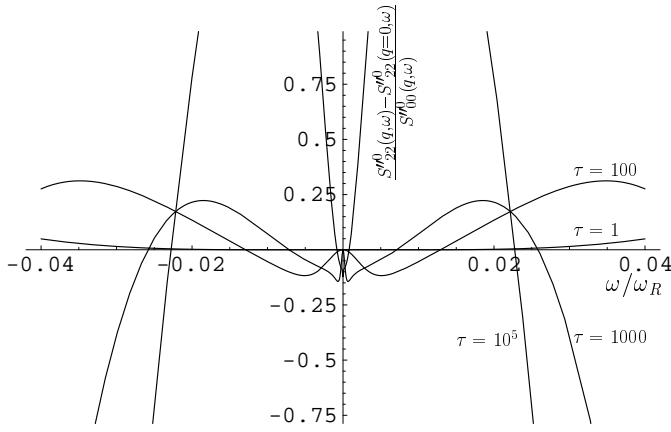


Fig. 14. The relation discussed in equation (13) is plotted on a linear scale.

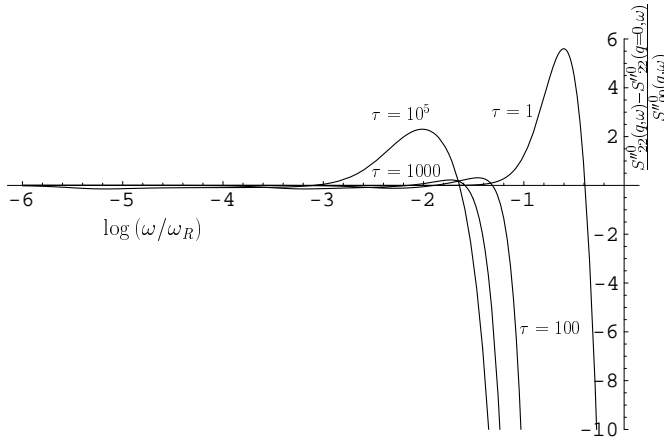


Fig. 15. The relation discussed in equation (13) is plotted on a logarithmic scale.

is no matrix element in the memory kernel which couples to the $m = 2$ component.

Similar to the $m = 1$ component the $m = 0$ component also shows a coupling of a hydrodynamic mode. However in this case it is the longitudinal phonon which couples into the $m = 0$ susceptibility. The spectral function of $\chi_{22}^0(q, z)$ on a logarithmic frequency scale is plotted in Figure 11.

The overall situation for a fictitious spectrum $\omega I^{VV}(q, \omega)$ is shown in Figure 13 for the same parameters as in Figure 12. Note that due to the mixture of $l = l' = 0$ and $l = l' = 2$ components the Brillouin line of the longitudinal phonon consists of two components. One is caused by the direct observation of the center of mass component where the longitudinal phonon gives a low lying microscopic frequency whereas the other contribution comes from the phonon mode coupling into the $l = l' = 2$, $m = 0$ component.

4.4 Light-scattering near an orientational instability

Further physics which is contained already in equation (32) are some aspects of light scattering near an orientational instability (*e.g.* near an isotropic-nematic transition). From equation (32) one can see that the amplitude of the light scattering intensity is for the depolarized light scattering spectra mainly given by the static density correlation $S_{22}^m(q)$. Close to a nematic transition, a weakly first order phase transition, $S_{22}^m(q)$ increases strongly for small q where $\lim_{q \rightarrow 0} S_{22}^m(q)^{-1} = \kappa_{\text{Kerr}}$ is the optical Kerr constant. On the other hand the rotational frequency ω^R (in Eq. (36)) contains $S_{22}^m(q)^{1/2}$ in the denominator. In this way our equations describe the broad central peak together with the strong scattering intensities at the isotropic-nematic transition.

5 Relation to other theories

The main issue of the paper so far, was to demonstrate that the theory of light scattering can be brought in a form, which is accessible to tested theories for the dynamics of supercooled molecular liquids and to show that the structure of the equations of motion reproduce the light scattering experiments for molecular liquids. We now will show how the phenomenological equations underlying the most recent theory of light scattering for molecular liquids [13] can be rigorously derived within our theory. To keep the derivation as simple as possible, we will restrict ourselves to the variables $\rho_{00}, \rho_{2m}, \{j_\mu^T\}_{00}, \{j_0^R\}_{2m}$ used in Section 4. We also will comment on [12] and on [14]. In Appendix A we demonstrate for the theory of Anderson and Pecora [5] how light scattering theories for linear molecules based on projection operator formalisms can be related to our theory.

Dreyfus *et al.* [13] start by writing the continuity equations for the center of mass density fluctuations and the center of mass momentum density fluctuations,

$$\frac{\partial}{\partial t} \rho_{00}(q, t) = i\mathbf{q}\mathbf{j}(q, t) \quad (57)$$

$$\frac{\partial}{\partial t} j_i(q, t) = iq_j \sigma_{ji}(q, t), \quad (58)$$

where j_i are the Cartesian components of the center of mass current fluctuations and σ_{ij} are the Cartesian components of the stress-fluctuations. To obtain a closed set of equations it is necessary to write down constitutive equations for the stress-fluctuations which relate them to the current and density fluctuations. Instead of using phenomenological ansatzes, as it was mostly done in the existing literature, we will write down exact equations for the stress-tensor fluctuations using generalized constitutive equations. By using a formalism introduced in [33] we can express the stress-fluctuations for vanishing amplitude of the wave-vector exactly by the fluctuations of the basic set of variables, which we used in Section 4 (for

simplicity it is more convenient to use the Cartesian components of the center of mass current fluctuations)

$$\begin{aligned} \sigma_{ij} = & \rho_{00}(\mathbf{q}, t) \frac{1}{S_{00}^0(q=0)} (\rho_{00}|\sigma_{ij}) \\ & + i j_r(\mathbf{q}, t) q_k \otimes \frac{m}{N k_B T} (\sigma_{rk}|R'(t)|\sigma_{ij}) \\ & + i \{j_0^R\}_{2m}(\mathbf{q}, t) \otimes \frac{\Theta}{N k_B T} (\mathcal{L}\{j_0^R\}_{2m}|R'(t)|\sigma_{ij}). \end{aligned} \quad (59)$$

Here, repeated indices are summed over and we defined $A \otimes B = \int_0^t dt' A(t')B(t-t')$. $R'(t)$ is again the reduced time propagator acting in the space perpendicular to the chosen density and current fluctuations. Therefore no terms of the form $(\mathcal{L}\rho_{lm}|R'(t)|\sigma_{ij})$ appear in equation (59). There are in principal terms proportional to the fluctuations ρ_{2m} . But since in equation (57) only the combination $q_j \sigma_{ji}$ appears, the proportionality factor contains the term $q_j (\rho_{2m}|\sigma_{ji}) = (\rho_{2m}|\mathcal{L}j_i) = (\mathcal{L}\rho_{2m}|j_i) = \sqrt{6} (\{j_0^R\}_{2m}|j_i) = 0$ [1]. Therefore no fluctuations proportional to ρ_{2m} do contribute to the generalized hydrodynamic equations. For $q \rightarrow 0$ the equations (59) considerably simplify. The only symmetric tensor of rank four $(\sigma_{rk}|R'(t)|\sigma_{ji})$, which does not vanish for $q \rightarrow 0$ is $(\sigma_{rk}|R'(t)|\sigma_{ji}) = (p|R'(t)|p)\delta_{kr}\delta_{ij} + (\sigma_{ij}^s|R'(t)|\sigma_{ij}^s)(\delta_{rj}\delta_{ki} + \delta_{ri}\delta_{kj} - \frac{2}{3}\delta_{ij}\delta_{rk})$, where $p = \frac{1}{3}\sum_i \sigma_{ii}$ is the scalar part and σ_{ij}^s the traceless part of the stress-tensor fluctuations. The third row of equations (59) can be evaluated by transforming σ_{ij} to spherical components σ_{lm} . Then, for $q \rightarrow 0$, the identity $\{j_0^R\}_{2m}|R'(t)|\sigma_{lm'} = \delta_{l2}\delta_{mm'}(\mathcal{L}\{j_0^R\}_{20}|R'(t)|\sigma_{20})$ and $\dot{\rho}_{2m}(t) = \sqrt{6}\{j_0^R\}_{2m}(t)$ can be used. Therefore the constitutive equations (59) reduce to

$$\sigma_{ij} = \delta P(t)\delta_{ij} + \frac{\eta_B(t)}{n} \otimes \mathbf{ij}(t)\delta_{ij} \quad (60)$$

$$\begin{aligned} & + \frac{1}{n}\eta_S(t) \otimes \tau_{ij}(t) \\ & - \mu(t) \otimes \dot{Q}_{ij}(t). \end{aligned} \quad (61)$$

with $\eta_B(t) = \frac{1}{k_B T V}(p|R'(t)|p)$, $\eta_S(t) = \frac{1}{k_B T V} \times (\sigma_{ij}^s|R'(t)|\sigma_{ij}^s)$ being the generalized bulk viscosity and shear viscosity, respectively [33]. The tensor $\tau_{ij} = i(q_i j_j + q_j j_i - \frac{2}{3}\mathbf{qj}\delta_{ij})$ is the strain tensor. The fluctuations $\delta P(t)$ of the internal hydrostatic pressure due to density fluctuations are given by $K\rho_{00}(q, t)$, where $K = \frac{k_B T}{S_{00}^0(q=0)}$ is the (static) bulk module, *i.e.* the inverse of the compressibility κ . The tensor Q is given by

$$\frac{1}{\sqrt{6}} \begin{pmatrix} -\frac{\rho_{20}}{\sqrt{6}} + \frac{\rho_{22}}{2} + \frac{\rho_{2\bar{2}}}{2} & -i\frac{\rho_{22}}{2} + i\frac{\rho_{2\bar{2}}}{2} & -\frac{\rho_{21}}{2} + \frac{\rho_{2\bar{1}}}{2} \\ -i\frac{\rho_{22}}{2} + i\frac{\rho_{2\bar{2}}}{2} & -\frac{\rho_{20}}{\sqrt{6}} - \frac{\rho_{22}}{2} - \frac{\rho_{2\bar{2}}}{2} & i\frac{\rho_{21}}{2} + i\frac{\rho_{2\bar{1}}}{2} \\ -\frac{\rho_{21}}{2} + \frac{\rho_{2\bar{1}}}{2} & i\frac{\rho_{21}}{2} + i\frac{\rho_{2\bar{1}}}{2} & \sqrt{\frac{2}{3}}\rho_{20} \end{pmatrix} \quad (62)$$

and the function $\mu(t)$ is the the matrix element $\mu(t) = \frac{-\theta}{k_B T N}(\mathcal{L}\{j_0^R\}_{20}|R'(t)|\tau_{20})$. Now we only need another constitutive equation for the tensor $Q_{ij}(t)$. Using the same

strategy as in the derivation of the constitutive equations for the stress tensor we easily derive

$$\begin{aligned} \frac{d^2}{dt^2} Q_{ij}(t) = & -\omega_R^2 Q_{ij}(t) + \mu(t) \otimes \tau_{ij}(t)r \\ & - \{M_{00}^{RR}\}_{22}^{00}(t) \otimes \dot{Q}_{ij}(t) \end{aligned} \quad (63)$$

where $r = \frac{m}{\Theta}$. Here the same function $\mu(t)$ as in equation (60) appears naturally within the formalism, confirming the Onsager principle. The memory-function $\{M_{00}^{RR}\}_{22}^{00}(t)$ is the same as used in Section 3. equations (57–63) are exactly the equations used in [13]. With our formalism, we can identify the phenomenologically introduced functions $\mu(t)$ and $Q_{ij}(t)$ of [13]. We also want to emphasize, that the convolution integrals in time *i.e.* the retardation effects are a necessary consequence of the slowing down of structural relaxations and its effect on the frequency dependent viscosities and the rotation-stress coupling function $\mu(t)$. The ansatz of Quentrec [8], where the viscosities and $\mu(t)$ are replaced by only temperature dependent functions is therefore not acceptable for the description of supercooled liquids.

It is important to note, that the form of the equations (57–59) depends crucially on the chosen set of variables. If we would *not* have chosen the rotational currents $\{j_0^R\}_{2m}(\mathbf{q}, t)$ explicitly as a member of our basic set of equations the last line of equation (60) would contain a coupling $\hat{\mu}(t) \otimes Q_{ij}(t)$ to the tensor Q_{ij} instead of to its time derivative. The function $\hat{\mu}(t)$ can also be expressed in terms of a (modified) reduced time propagator $\hat{R}(t)$, $\hat{\mu}(t) \propto (\{j_0^R\}_{20}|\hat{R}(t)|\tau_{20})$. In addition, the equation for $Q_{ij}(t)$ were of first order in time instead of second order. Wang uses a mixed representation [12]. His constitutive equation for the stress tensor coincides with equation (59), but the equation for Q_{ij} is only of first order. For deriving exactly such a set of equations, it were necessary to use different projection operators for deriving the constitutive equation and the equation for the tensor Q_{ij} . From our point of view there are mainly two reasons why it seems more advantageous to choose one single set of basis variables including the currents $\{j_0^R\}_{2m}(\mathbf{q}, t)$. First, approximation schemes for force-force autocorrelation functions *i.e.* the memory-function $\{M_{\mu\mu'}^{\alpha\alpha'}\}_{ll'}^{mm'}(t)$ seem to be easier, than for mixed current-force memory-functions, which would appear, when only the densities $\rho_{lm}(\mathbf{q}, t)$ and the conserved currents $\{j_\mu^T\}_{lm}(\mathbf{q}, t)$ were used as variables. Second, by using one set of variables the Onsager relations are automatically fulfilled, since there appears the same function $\mu(t)$ in the equation for the stress and the tensor $Q_{ij}(t)$. In the approach of Wang it is important to choose the approximations for the different functions $\hat{\mu}(t)$ and $\mu(t)$ carefully, such that the Onsager principle is guaranteed. (Essentially the time derivative of $\hat{\mu}(t)$ is related to $\mu(t)$.)

The approach of [14] is more general than ours, since no assumptions on the scattering mechanisms were used to derive the general form of light scattering spectra of supercooled liquids. This was achieved by only using the hydrodynamic variables center of mass density and center of mass currents as the basic set of variables for applying

constitutive equations to the dielectric tensor fluctuations. In this way the coupling mechanisms between rotation and translations in molecular liquids are not explicitly treated but lead implicitly to frequency dependent Pockels constants, relating the hydrodynamic modes to the dielectric tensor fluctuations, and unknown background spectra. Due to the general nature of the approach in principle also other mechanisms like DID are contained on a formal level in the description, although they cannot be explicitly treated without using a specific theory.

In our approach we concentrated on a specific mechanism for the coupling of light to the motion of the linear molecules, by assuming that the principal axis of the polarizability tensor agree with the principal axis of the inertia tensor of the molecule. Under this assumption equations (7) and (8) are completely general. The importance of the index of helicity m seems to be at variance with the approach of [14], since there only $m = 0$ components appear. But if we express $S_{22}^m(q, t)$ by correlation functions of the hydrodynamic variables plus a background spectra with the help of the exact generalized constitutive relations as used above we obtain in the q -frame for $q \rightarrow 0$

$$\begin{aligned} S_{22}^m(z) &= (\rho_{2m}|R'^{\text{NH}}(z)|\rho_{2m}) \\ &+ q^2((\rho_{2m}|R'^{\text{NH}}(z)|\sigma_{zz})\frac{m}{k_{\text{B}}T})^2(j_{\parallel}|R(z)|j_{\parallel}) \\ &+ 2q^2((\rho_{2m}|R'^{\text{NH}}(z)|\sigma_{xz})\frac{m}{k_{\text{B}}T})^2(j_{\perp}|R(z)|j_{\perp}). \end{aligned} \quad (64)$$

Here the reduced resolvent $R'^{\text{NH}}(z) = \frac{-Q}{z-Q\mathcal{L}Q}$ describes the dynamic perpendicular to the hydrodynamic fluctuations only *i.e.* the subscript NH indicates, that the projection operator Q , used in equation (64) projects on the space of non hydrodynamic variables. Transforming σ_{ij} to irreducible spherical components, the I^{VH} spectrum (8) can be written

$$I^{\text{VH}}(z) = \mathcal{T}(z) - q^2 \cos^2(\Theta/2) a_{\text{VH}}^2(z) (j_{\perp}|R(z)|j_{\perp}) \quad (65)$$

where the background spectrum $\mathcal{T}(z)$ and the generalized Pockels constant $a_{\text{VH}}(z)$ are given by

$$\begin{aligned} \mathcal{T}(z) &= g^2 \frac{4\pi}{15} (\rho_{20}|R'^{\text{NH}}(z)|\rho_{20}) \\ a_{\text{VH}}(z) &= g \sqrt{\frac{4\pi}{15}} (\rho_{20}|R'^{\text{NH}}(z)|\sigma_{20}) \frac{m}{k_{\text{B}}T}. \end{aligned} \quad (66)$$

In leading order in q (*i.e.* $q \equiv 0$) we are now allowed to replace the reduced resolvent in equation (66) with the full resolvent [14]. Similar equations can be derived for the I^{VV} spectrum. Equation (65) is exactly the form found in [14]. The explicit m dependence is not present anymore in (65), since we used that at $q = 0$ correlation functions between fluctuations with the same l and m , which do not contain hydrodynamic poles, do not depend on m anymore. But it is important to note, that the dynamic coupling to the transversal current fluctuations is not vanishing, only due to the existence of an irreducible $m = 1$ component of the stress tensor. Also in [14] this symmetry

was implicitly used. But after using it, the reduced matrix element $(\rho_{21}|R'^{\text{NH}}(z)|\sigma_{21})$ can be replaced by the one for $m = 0$ at $q = 0$ in equation (64). The m dependence is replaced by an explicit dependence on the transversal current spectrum, which is only present due to the coupling of $S_{22}^1(q, z)$ to the transversal current fluctuations. We could now further proceed and express the background spectrum and the Pockels constant with the method, explained in the Appendices A and B, by the correlation functions and memory functions, which we used in Sections 3 and 4. But since we have to evaluate the center of mass current correlation functions and the center of mass density correlation function at small but finite values of q (for example to be able to understand the renormalization of the transversal sound waves by rotation translation coupling), we would arrive at exactly the same theory, which we already derived in the mentioned sections. The merit of the approach of [14] is to work out the most general form of light scattering spectra using only generalized hydrodynamic and generalized constitutive equations for dielectric fluctuations. Thus rigorous constraints concerning the appearance of hydrodynamic excitations in different scattering geometries are formulated. For explicit considerations of specific scattering mechanisms, as done in this paper, one has in general to include also non hydrodynamic variables.

6 Conclusion

In this work we developed a microscopic theory of light scattering for linear molecules, concentrating on the direct contribution to the spectra. The starting point of our theory is an exact expression for the spectra in terms of correlation functions (Eqs. (7) and (8)). It turns out to be important to accurately take the tensorial character of the orientational correlation function into account. This is due to the fact that the orientational components of different helicity index m transform in general differently under rotations. It is in this context crucial, that the dynamic correlation functions $S_{22}^m(q, \omega)$ (contrary to the memory functions) have to be evaluated at small but *finite* wave vectors due to the following reason. The rotational symmetry allows for the dynamic coupling of $m = 0$ components of tensorial densities ρ_{lm} and rotational currents to the longitudinal and the $m = 1$ components of tensorial densities ρ_{lm} and rotational currents to transversal current fluctuations, respectively. Microscopically the coupling is non vanishing due to the induction of local stress by the rotation of the molecules. Therefore the hydrodynamic poles show up in the corresponding dynamic correlation function $S_{22}^m(q, \omega)$. Thus we are not allowed to replace them by their value at $q = 0$, where indeed correlation functions for different values of m , but the same l , are equal. Only the $m = 2$ component of $S_{22}^m(q, \omega)$ which does not couple to any hydrodynamic mode and all memory functions, which – due to our choice of dynamic variables – do not contain by construction any hydrodynamic pole, can be replaced by its value at $q = 0$. It is the violation of rotational symmetry on the spatial scale of the light scattering

experiments due to the existence of hydrodynamic modes, which causes the importance of the helicity index m .

Based on a projection operator formalism, we formulate a microscopic theory for the correlation functions $S_{ll}^m(q, \omega)$ of supercooled molecular liquids, which include all possible couplings to hydrodynamic modes. Simplifying the equations of the molecular mode coupling theory extended by transverse currents, we demonstrate explicitly, that a qualitative description for light scattering spectra near the glass transition can be achieved, which treats correctly the interplay of hydrodynamic modes and structural relaxations. We further derive microscopic expressions which give the influence of the rotation-translation coupling onto the hydrodynamic poles. It is also shown how other theories of light scattering can be expressed by the quantities, which appear in our theory.

The equations (7) and (8) are in principle not restricted to small q -values. They are therefore also valid for the interpretation of X-ray spectra, if we give up the restriction to small wave vectors. Since the MMCT, formulated in our paper is a theory for all wave vectors, there will be no principal problems to do this. A possible application of the restricted theory in Section 4, would be to compare spectra of different scattering angles and of different scattering geometries in order to obtain microscopically relevant quantities like *e.g.* the rotation-translation coupling. But to obtain reliable results, it is of course necessary to give up the Maxwell ansatz and to include β relaxation phenomena in the memory functions. Further we like to encourage the evaluation of the orientational components for different m values from computer simulations.

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Appendix A: Coupling between polarizability and shear stress

To demonstrate how theories of light-scattering, based on various projection operator formalism can in principal be expressed by the correlation functions appearing in molecular MCT, we take as an example the set of variables from the book of Berne and Pecora [22] and show how their memory functions can be evaluated using the basis set of molecular MCT.

We use the projection operator formalism in Laplace transformed space (see *e.g.* [34]). To explain the appearance of a Rytov Dip, in [22] the polarizability and one component of the transverse current $j_x(q, z)$ with $j_x \sim 1/\sqrt{2}(\{j_1^T\}_{00} + i\{j_{-1}^T\}_{00})$ are chosen as a minimal basis set. $z = \omega + i\epsilon$ is the complex frequency. We have shown in Section 2 that the polarizability for the depolarized light

scattering is in the subspace of the $l = 2$ density. Therefore we define $\alpha_{\text{VH}}(q, z) =: \rho_2 = \sum_m B_m \rho_{2m}$. Applying Mori-Zwanzig projection technique with a projection operator $P_{\text{BP}} = |\rho_2\rangle \frac{1}{(\rho_2|\rho_2)} (\rho_2| + |j_x\rangle \frac{1}{(j_x|j_x)} (j_x|)$ and $Q_{\text{BP}} = \underline{1} - P_{\text{BP}}$, the dynamics of the polarizability correlation function for the depolarized light scattering results from a solution of the following 2×2 matrix equation:

$$\begin{pmatrix} z - (\rho_2 \mathcal{L} R'_1 \mathcal{L} \rho_2) & -(\rho_2 \mathcal{L} R'_1 \mathcal{L} j_x) \\ - (j_x \mathcal{L} R'_1 \mathcal{L} \rho_2) & z - (j_x \mathcal{L} R'_1 \mathcal{L} j_x) \end{pmatrix} \times \begin{pmatrix} (\rho_2 \rho_2)(q, z) \\ 0 \end{pmatrix} = \begin{pmatrix} (\rho_2 \rho_2)^0 \\ 0 \end{pmatrix} \quad (\text{A.1})$$

which is still exact. \mathcal{L} is the Liouvillian and $R'_1 = Q_{\text{BP}}(z - Q_{\text{BP}} \mathcal{L} Q_{\text{BP}})^{-1} Q_{\text{BP}}$ is the reduced dynamics and $(\rho_2 \rho_2)^0$ is the static correlation function. The occurrence of a dip in the spectrum relies on the fact that the off diagonal element $(\rho_2 \mathcal{L} R'_1 \mathcal{L} j_x)$ does not vanish for small but finite wave-vector q . It follows from momentum conservation, that it is of order q . It is therefore possible to define an effective coupling constant R between transversal current fluctuations and polarizability fluctuations due to the rotation of the molecule (see Ref. [22] p. 317 to have an explicit connection between the phenomenological theory in [22] based on an incomplete basis set for the projection technique and our microscopic theory)

$$R \sim \lim_{z \rightarrow 0 + i\epsilon} \lim_{q \rightarrow 0} \frac{1}{q^2} |(\rho_2 \mathcal{L} R'_1 \mathcal{L} j_x)|^2 \neq 0. \quad (\text{A.2})$$

In the following we show, how this matrix element can be expressed by the memory-functions of MMCT. In this theory not only the density ρ_{2m} , but also the corresponding currents $\{j_0^\alpha\}_{2m}$ are used as additional variables. A coupling of the form equation (A.2) can therefore not appear since the reduced resolvent R'_2 in the new set of variables is projecting perpendicular to the currents *i.e.* also perpendicular to $\mathcal{L} \rho_2$ as defined above. We have shown in detail in Section 4:

$$\begin{aligned} \mathcal{L} \rho_2 &= \sum_m B_m \mathcal{L} \rho_{2m}(q, z) = \sum_m B_m q \{j_0^T\}_{2m}(q, z) \\ &\quad + \sqrt{2(2+1)} \{j_0^R\}_{2m}(q, z) \\ &= \sum_m B_m \sqrt{2(2+1)} \{j_0^R\}_{2m}(q, z) + O(q) \\ &=: j_2 \end{aligned} \quad (\text{A.3})$$

where T refers to translational currents which occur when applying the Liouvillian on the time dependent positions and R refers to rotational currents which appear when applying the Liouvillian to the time dependent orientations. For small wave-vectors, we can neglect the contribution of translational currents in the following analysis. We also showed in Section 4, that only the $m = 1$ component of the rotational current $\mathcal{L} j_2$ has non-vanishing matrix elements with $\mathcal{L} j_x$. Applying again Mori-Zwanzig projection technique with the enlarged Hilbert space with

$$P_L = |\rho_2\rangle (\rho_2| + |j_x\rangle (j_x| + |j_2\rangle (j_2|) \quad (\text{A.4})$$

and $Q_L = \underline{1} - P_L$ leaves a 3×3 matrix equation to be solved. Note that due to equation (A.3) contributions that contain $Q_L \mathcal{L} \rho_2$ vanish.

$$\begin{pmatrix} z & & -(\rho_2 \mathcal{L} j_2) \\ & z - (j_x \mathcal{L} R'_2 \mathcal{L} j_x) & -(j_x \mathcal{L} R'_2 \mathcal{L} j_2) \\ - (j_2 \mathcal{L} \rho_2) & - (j_2 \mathcal{L} R'_2 \mathcal{L} j_x) & z - (j_2 \mathcal{L} R'_2 \mathcal{L} j_2) \end{pmatrix} \times \begin{pmatrix} (\rho_2 \rho_2)(q, z) \\ 0 \\ 0 \end{pmatrix} = \begin{pmatrix} (\rho_2 \rho_2)^0 \\ 0 \\ 0 \end{pmatrix} \quad (\text{A.5})$$

here R'_2 is the reduced dynamics due to the new variable set:

$$R'_2 = Q_L (z - Q_L \mathcal{L} Q_L)^{-1} Q_L. \quad (\text{A.6})$$

Making an additional projection step to obtain an effective 2×2 -matrix with $|\rho_2\rangle$ and $|j_x\rangle$ as variables (see Appendix B) gives a theory for the matrix elements of equation (A.1):

$$\begin{aligned} (\rho_2 \mathcal{L} R'_1 \mathcal{L} \rho_2) &= \frac{|(\rho_2 \mathcal{L} j_2)|^2}{z - (j_2 \mathcal{L} R'_2 \mathcal{L} j_2)} \\ (j_x \mathcal{L} R'_1 \mathcal{L} j_x) &= (j_x \mathcal{L} R'_2 \mathcal{L} j_x) + \frac{|(j_x \mathcal{L} R'_2 \mathcal{L} j_2)|^2}{z - (j_2 \mathcal{L} R'_2 \mathcal{L} j_2)} \\ (j_x \mathcal{L} R'_1 \mathcal{L} \rho_2) &= \frac{(j_x \mathcal{L} R'_2 \mathcal{L} j_2)(j_2 \mathcal{L} \rho_2)}{z - (j_2 \mathcal{L} R'_2 \mathcal{L} j_2)}. \end{aligned} \quad (\text{A.7})$$

The transformation to the complete set of variables used in MMCT involves inversions of much larger matrices, but the strategy will be the same. For $q \rightarrow 0$ only the matrix elements in equation (A.7) should be relevant. equation (A.7) together with the mode coupling expressions in Section 3, therefore constitute a microscopic theory for the effective coupling coefficient equation (A.2) of the theory described in [22].

Appendix B: Connection between different projection schemes

Let us assume we have a particular basis system A_i, B_k with $(B_i | A_k) = 0$ for all i, k , which spans the subspace \mathcal{H}^L . An example for that would be the basis set of MMCT described in Section 3, with A_i being the densities ρ_{lm} and B_k the currents $\{j_\mu^\alpha\}_{lm}$. With such a basis set of the Hilbert space a projection operator \hat{P}^L can be defined, which projects into the subspace \mathcal{H}^L . Within the subspace \mathcal{H}^L we have a theory to calculate the matrix elements of the memory function. In order to be able to compare different projection schemes using a reduced set of variables A_i , which are elements of a subspace $\mathcal{H}^A \subset \mathcal{H}^L$ we need a formalism which expresses all matrix elements in the subspace \mathcal{H}^A as functions of the matrix elements in the subspace \mathcal{H}^L . This can be achieved by applying a formalism described in [33].

In \mathcal{H}^L the operator $(z - \mathcal{L})^{-1}$ is given by:

$$\begin{aligned} \hat{P}^L (z - \mathcal{L})^{-1} \hat{P}^L &= \left[\hat{P}^L (z - \mathcal{L}) \hat{P}^L - \hat{P}^L \mathcal{L} \hat{Q}^L \right. \\ &\quad \left. \times (\hat{Q}^L (z - \mathcal{L}) \hat{Q}^L)^{-1} \hat{Q}^L \mathcal{L} \hat{P}^L \right]^{-1} \\ &= \left[\hat{P}^L (z - \mathcal{L}) \hat{P}^L - \hat{P}^L \mathcal{L} \hat{R}^{L'} \mathcal{L} \hat{P}^L \right]^{-1} \end{aligned} \quad (\text{B.1})$$

where $\hat{Q}^L = \hat{1} - \hat{P}^L$ is the usual projector perpendicular to \hat{P}^L and $\hat{R}^{L'}$ is the reduced dynamics.

Due to the orthogonality of the variables A_i, B_k we can decompose \hat{P}^L in $\hat{P}^L = \hat{P}^A + \hat{P}^B$ such that $\hat{Q}^L + \hat{P}^B = \hat{1} - \hat{P}^A$. In the subspace \mathcal{H}^A we can write down a similar equation as above:

$$\hat{P}^A (z - \mathcal{L})^{-1} \hat{P}^A = \left[\hat{P}^A (z - \mathcal{L}) \hat{P}^A - \hat{P}^A \mathcal{L} \hat{R}^{A'} \mathcal{L} \hat{P}^A \right]^{-1} \quad (\text{B.2})$$

where the reduced dynamics is in the subspace \mathcal{H}^A is given by

$$\hat{R}^{A'} = \hat{Q}^A \left[\hat{Q}^A (z - \mathcal{L}) \hat{Q}^A \right]^{-1} \hat{Q}^A. \quad (\text{B.3})$$

Let us now express $\hat{R}^{A'}$ depending on the reduced dynamics $\hat{R}^{L'}$. We will therefore have to do an inversion of the operator $\hat{M} := (\hat{Q}^A (\mathcal{L} - z) \hat{Q}^A)$

$$\hat{M} = \begin{pmatrix} \hat{P}^B (\mathcal{L} - z) \hat{P}^B & \hat{P}^B (\mathcal{L} - z) \hat{Q}^L \\ \hat{Q}^L (\mathcal{L} - z) \hat{P}^B & \hat{Q}^L (\mathcal{L} - z) \hat{Q}^L \end{pmatrix}. \quad (\text{B.4})$$

The inversion of \hat{M} gives [33]:

$$\hat{M}^{-1} = \hat{R}^{A'} = \hat{R}^{L'} - (\hat{P}^B - \hat{R}^{L'} \hat{M}) \hat{K} (\hat{M} \hat{R}^{L'} - \hat{P}^B) \quad (\text{B.5})$$

with

$$\hat{K} = \left(\hat{P}^B (-z + \mathcal{L}) \hat{P}^B - \hat{P}^B \mathcal{L} R^{L'} \mathcal{L} \hat{P}^B \right)^{-1}. \quad (\text{B.6})$$

Therefore the connection between the two reduced dynamics R^A and $R^{L'}$ are given by:

$$\hat{R}^{A'} = \hat{R}^{L'} - (\hat{P}^B - \hat{R}^{L'} \mathcal{L} \hat{P}^B) \hat{K} (\hat{P}^B \mathcal{L} \hat{R}^{L'} - \hat{P}^B). \quad (\text{B.7})$$

This connection was used in equation (A.7) to derive the connection between the dynamics in the two different basis sets.

Appendix C: Matrix elements of the polarizability tensor

The polarizability of every molecule equation (2) is a tensor of rank 2. It can be written as a scalar plus an irreducible tensor of rank 2. In a body fixed coordinate

$$\alpha^S(t) = a \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} + 2g\sqrt{\frac{2\pi}{15}} \begin{pmatrix} -\frac{1}{\sqrt{6}}Y_{20}(\Omega(t)) + \text{Re}(Y_{22}(\Omega(t))) & \text{Im}(Y_{22}(\Omega(t))) & -\text{Re}(Y_{21}(\Omega(t))) \\ \text{Im}(Y_{22}(\Omega(t))) & -\frac{1}{\sqrt{6}}Y_{20}(\Omega(t)) - \text{Re}(Y_{22}(\Omega(t))) & -\text{Im}(Y_{21}(\Omega(t))) \\ -\text{Re}(Y_{21}(\Omega(t))) & -\text{Im}(Y_{21}(\Omega(t))) & \sqrt{\frac{2}{3}}Y_{20}(\Omega(t)) \end{pmatrix} \quad (\text{C.6})$$

system, with \hat{n}^i chosen along the principal axis, it has the simple form:

$$\alpha^B = a \begin{pmatrix} 1 & & \\ & 1 & \\ & & 1 \end{pmatrix} + \frac{2g}{3} \begin{pmatrix} -\frac{1}{2} & & \\ & -\frac{1}{2} & \\ & & 1 \end{pmatrix}. \quad (\text{C.1})$$

The irreducible spherical components are calculated by:

$$\alpha_{lm} = \sum_{i,j} \sum_{m_1, m_2} C(11l; m_1 m_2 m) U_{m_1 i} U_{m_2 j} \alpha_{ij}^B \quad (\text{C.2})$$

where the $i, j \in \{x, y, z\}$ are Cartesian indices and $m_1, m_2 \in \{-1, 0, 1\}$ are spherical ‘‘helicity’’ indices. $C(l_1 l_2 l; m_1 m_2 m)$ are the Clebsch Gordan coefficients. The matrix U is given by

$$U_{mi} = \begin{pmatrix} \frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ -\frac{1}{\sqrt{2}} & -\frac{i}{\sqrt{2}} & 0 \end{pmatrix}. \quad (\text{C.3})$$

In the body fixed frame α^B only the spherical components α_{lm}^B with $m = 0$ do not vanish: $\alpha_{00}^B = -\sqrt{3} a$ and $\alpha_{20}^B = \sqrt{\frac{2}{3}} g$. The spherical components in the q -frame are easily obtained by rotation.

$$\alpha_{lm}^S(\hat{\Omega}_i(t)) = \sum_n D_{nm}^l(\Omega_i^{-1}(t)) \alpha_{ln}^B = D_{m0}^l(\Omega_i(t))^* \equiv \sqrt{\frac{4\pi}{2l+1}} Y_{lm}(\Omega_i(t)) \quad (\text{C.4})$$

where $D_{nm}^l(\Omega_i(t))$, $Y_{lm}(\Omega_i(t))$ are the Wigner matrices and spherical harmonics, respectively. We used, that the angle $\hat{\Omega}_i(t)$ denotes the rotation carrying the body fixed frame into coincidence with the space fixed q -frame. This is the inverse $\hat{\Omega}_i(t) = \Omega^{-1}(t)$ to the angle describing the orientation of the molecules with respect to the q -frame. The Cartesian components in the q -frame are obtained by applying the inverse transformation to (C.2)

$$\alpha_{ij}^S = \sum_{lm} \sum_{m_1, m_2} U_{im_1}^{-1} U_{jm_2}^{-1} C(11l; m_1 m_2 m) \alpha_{lm}^S. \quad (\text{C.5})$$

The final result for α^S is:

see equation (C.6) above

where Im, Re denote imaginary and real part, respectively,

From the matrix element of equation (C.6) and equations (5, 6) we can calculate the contributions which are

observable in different scattering geometries. Due to the fact that we use the q -frame as the external coordinate system the correlation function $S_{ll'}^{mm'}$ are diagonal with respect to m, m' and $S_{ll'}^m(q, t) = S_{ll'}^{-m}(q, t)$. With

$$\begin{aligned} \frac{N}{2} S_{22}^m(q, t) &= \sum_{i,j} \langle \text{Im} Y_{2m}(\Omega_i(t)) e^{-i\mathbf{q}\mathbf{r}_i(t)} \text{Im} Y_{2m}(\Omega_j(0)) e^{i\mathbf{q}\mathbf{r}_j(0)} \rangle \\ &= \sum_{i,j} \langle \text{Re} Y_{2m}(\Omega_i(t)) e^{-i\mathbf{q}\mathbf{r}_i(t)} \text{Re} Y_{2m}(\Omega_j(0)) e^{i\mathbf{q}\mathbf{r}_j(0)} \rangle \end{aligned}$$

and

$$\begin{aligned} \delta_{m,0} \frac{N}{2} S_{21}^0(q, t) &= \sum_{i,j} \langle \text{Re} Y_{2m}(\Omega_i(t)) e^{-i\mathbf{q}\mathbf{r}_i(t)} Y_{10}(\Omega_j(0)) e^{i\mathbf{q}\mathbf{r}_j(0)} \rangle \end{aligned}$$

the results (7, 8) are obtained.

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