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HYDRODYNAMICS AND MOLECULAR MOTION: A PHENOMENOLOGICAL APPROACH

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A series of phenomenological macro–micro correlations is developed for single and multiparticle correlation functions descriptive of molecular rototranslation. The relation between hydrodynamic and molecular theories of molecular motion may then be investigated in the Markov limit. It is emphasised that a Mori continued fraction for non-Markov statistics and molecular motion on the single particle level is inconsistent with the unmodified viscoelastic approach exemplified by Bixon and Zwanzig. The analytical autocorrelation function must be related to a multimolecule correlation function via a macro–micro relation before comparison with the hydrodynamic theories is fruitful.

1. Introduction

Many of the theories developed for molecular motion in condensed phases are single particle in nature, i.e. they deal with autocorrelation functions alone[1–5]). However, in attempting to estimate these with spectroscopic data[6]) the problem is encountered of relating the autocorrelations and cross-correlations between different molecules. In dielectric relaxation[7]) the complex susceptibility is related to the orientational correlation function

$$C_{\mathrm{M}}(t)=\frac{1}{N^2}\sum\langle\boldsymbol{\mu}_i(0)\cdot\boldsymbol{\mu}_j(t)\rangle,$$

where $\boldsymbol{\mu}_i$ is the dipole vector on molecule i and N the total number of molecules. At $t=0$ the above equation may be identified with the g-factor of Kirkwood, which is important in mesophases[8]), where long-range order is encountered in the fluid state.

The historical method[4,9]) of describing dielectric relaxations in terms of a purely rotational, single-particle Langevin equation has disadvantages. For example:

(1) The high frequency behaviour of the dielectric spectrum is illdefined, essentially because memory effects and inertial effects are illdefined[10]).

(2) In reality the molecular motion is rototranslational[11]), a purely rotational description is unsubtle and its use obscures the mutual nuances of translation and rotation suggested by the computer simulators and the direct results of incoherent, inelastic neutron scattering[12]).

In this paper we aim to develop the simple theory to account for points (1) and (2) and within the same framework measure the mutual interaction of single molecule and collective rototranslation. In so doing we can calculate the extent of static and dynamic pair correlations between angular and linear momentum vectors fixed on different molecules. The angular momentum vector $\boldsymbol{J}$ is kinematically related to the dipole vector $\boldsymbol{\mu}$ so that a strong Kirkwood correlation of $\boldsymbol{\mu}$ implies that $\boldsymbol{J}$ is equally affected. A strong mutual correlation between linear momentum and orbital angular momentum on single molecule level intuitively leads to vorticity on the macroscopic scale. The propellor is a rough analogue.

The well-known Mori representation[13]) of the relevant equations of motion provides a means of linking hydrodynamic variables such as momentum density with molecular variables such as the momentum itself. The theory of light-scattering[1]) has been developed by mixing in this context the different hydrodynamic modes: particle, momentum, energy and spin density, vorticity, etc. We have recently[14]) used the matrix Mori theory in an entirely similar fashion to investigate rototranslation of individual molecules, or colloid particles. In section 2 we develop the Markovian single-particle (Langevin) theory of rototranslation for use on the macroscopic scale. A multidimensional approach due to Grigolini and co-workers[16]) is utilised in section 3 to generalise to non-Markovian statistics the results of section 2. Finally, in section 4 we discuss developments of the theory of sections 2 and 3, keeping in mind the possibility that the momentum and spin densities may couple to the energy and particle density, but only the coupling between angular momentum and linear momentum is relevant for the single particle motion. We show that, in principle, the dielectric spectrum contains information about mode–mode coupling in terms of various static and dynamic pair-correlations.

2. Markovian single-particle theory of rototranslation

The column vector $\boldsymbol{A}$ of arbitrary dynamical variables (assumed independent and which may also be other column vectors) is governed by the

Mori equation:

$$\dot{A}(t) = \mathrm{i}\Omega_A \cdot A(t) - \int_0^t \mathrm{d}\tau\, \phi_A(t-\tau) A(\tau) + \boldsymbol{F}_A(t). \tag{1}$$

Here $\mathrm{i}\Omega_A$ is a resonance frequency operator, the matrix kernel $\phi_A(t)$ is the effective Liouvillian (projected onto a subspace). $\boldsymbol{F}_A(t)$ is a stochastic variable with the units of force or torque, and propagated from $\boldsymbol{A}(0)$ via a projection operator technique. Denote by $\boldsymbol{A}_S(t)$ a column vector associated with the space rototranslation of a molecule j and by $\boldsymbol{A}_M(t)$ a column vector describing the cotemporal, many-molecule, collective motion engendered by $\boldsymbol{A}_S$ in the infinite past. We may define $\boldsymbol{A}_S$ by

$$\boldsymbol{A}_S = \begin{bmatrix} \boldsymbol{p}(t) \sum_n \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_n(t)} \\ \boldsymbol{\Omega}(t) \sum_n \mathrm{e}^{\mathrm{i}\boldsymbol{k}\cdot\boldsymbol{r}_n(t)} \end{bmatrix}. \tag{2}$$

Here $\boldsymbol{r}_n(t)$ is the position vector of the nth atom of the jth molecule, $\boldsymbol{p}(t)$ is the linear momentum of the jth molecule, $\boldsymbol{\Omega}(t)$ its angular momentum about a centre of mass reference. $\boldsymbol{k}$ is the wave vector associated with the transference of momentum from the measuring radiation to the system. In dielectric spectroscopy it is usually assumed that $\boldsymbol{k} \to \boldsymbol{0}$ in the final expressions for autocorrelations of $\boldsymbol{A}_S$ and $\boldsymbol{A}_M$. If there is no net mass flow the total linear momentum is conserved so that $\Sigma_j \boldsymbol{p}_j(t) = \boldsymbol{0}$. Then the velocity autocorrelation function and the cross-correlation function decay identically, since

$$\begin{aligned} \boldsymbol{v}_l(0) \cdot \sum_{j \neq l} \boldsymbol{v}_j(t) &= \boldsymbol{v}_l(0) \cdot \left(\sum_{j=1}^{N} \boldsymbol{v}_l(t) - \boldsymbol{v}_j(t) \right) \\ &= \boldsymbol{v}_l(0) \cdot \boldsymbol{v}_j(t). \end{aligned} \tag{3}$$

However, if there is a net mass flow the above relation is no longer valid. Also, the total molecular angular momentum density is conserved (spin plus orbital), but the spin and orbital densities are not conserved separately. We now define the spin density ($\boldsymbol{S}$) and current density ($\boldsymbol{g}$) Fourier components by

$$\boldsymbol{g}(t) = \sum_j \boldsymbol{p}_j(t) \sum_n \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_{n,j}(t)), \tag{4}$$

$$\boldsymbol{S}(t) = \sum_j \boldsymbol{\Omega}_j(t) \sum_n \exp(\mathrm{i}\boldsymbol{k} \cdot \boldsymbol{r}_{n,j}(t)) \tag{5}$$

and the vector $\boldsymbol{A}_M$ by

$$\boldsymbol{A}_M = \begin{bmatrix} \boldsymbol{g}(t) \\ \boldsymbol{S}(t) \end{bmatrix}. \tag{6}$$

Assuming that $\boldsymbol{k}$ is along the z-axis of the lab. frame then only the densities within the square brackets below take part in mode–mode mixing theory on the macroscopic level[17,18])

$$[g_x, S_y]; \quad [g_y, S_x]; \quad [S_z]; \quad [\rho, g_z, u]. \tag{7}$$

Here ρ is the particle density and u the energy density. The symmetry groupings (7) are valid only when there is no long-range ordering in the liquid and when the molecules have inversion symmetry. In a mesophase of chiral molecules (e.g. cholesteryl oleyl carbonate) a mixing of collective modes other than those defined in (7) is possible.

Having, for the sake of development, chosen the single particle rototranslation to be represented by $\mathbf{A}_\mathrm{S}$ and the collective rototranslation by $\mathbf{A}_\mathrm{M}$ we now deal with the problem of correlating $\mathbf{A}_\mathrm{S}$ and $\mathbf{A}_\mathrm{M}$ within the Mori framework. In section 4 we shall discuss other structures for $\mathbf{A}_\mathrm{M}$, but that will not affect the general theory set out below. It is convenient to define a vector orthogonal to $\mathbf{A}_\mathrm{S}$ by

$$\mathbf{A}_\mathrm{R} = \mathbf{A}_\mathrm{M} - \langle \mathbf{A}_\mathrm{M}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle\langle \mathbf{A}_\mathrm{S}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle^{-1}\mathbf{A}_\mathrm{S}, \tag{8}$$

where the superscript T denotes transpose, and solve, using the vector $\mathbf{A}_1 = \begin{bmatrix} \mathbf{A}_\mathrm{S} \\ \mathbf{A}_\mathrm{R} \end{bmatrix}$, eq. (1) for some interesting equilibrium time autocorrelation functions. It is convenient to make the following definitions:

(1) Define $P = 1 - Q$ as the projection operator onto the subspace $[\mathbf{A}_\mathrm{S}, \mathbf{A}_\mathrm{R}]$.

(2) Define the matrix $\boldsymbol{f}$ as

$$\boldsymbol{f} = \langle \mathbf{A}_\mathrm{S}^{(2)}\mathbf{A}_\mathrm{S}^{\mathrm{T}(1)}\rangle\langle \mathbf{A}_\mathrm{S}^{(1)}\mathbf{A}_\mathrm{S}^{(1)\mathrm{T}}\rangle^{-1}, \tag{9}$$

where $\mathbf{A}_\mathrm{S}^{(2)\mathrm{T}}$ refers to the vector of particle 2, and $\mathbf{A}_\mathrm{S}^{(1)}$ that of particle 1. The matrix $\boldsymbol{f}$ is that of the static pair correlations of distinct particles.

(3) Define the matrix $\mathbf{g}$ as

$$\mathbf{g} = \frac{\displaystyle\int_0^\infty \mathrm{d}t \langle \dot{\mathbf{A}}_\mathrm{S}^{(2)}(0)[\mathrm{e}^{\mathrm{i}Q\mathcal{L}t}\dot{\mathbf{A}}_\mathrm{S}^{(1)}(0)]^\mathrm{T}\rangle}{\displaystyle\int_0^\infty \mathrm{d}t \langle \dot{\mathbf{A}}_\mathrm{S}^{(1)}(0)[\mathrm{e}^{\mathrm{i}Q\mathcal{L}t}\dot{\mathbf{A}}_\mathrm{S}^{(1)}(0)]^\mathrm{T}\rangle} \tag{10}$$

i.e. that of the dynamical pair correlations.
We have

$$\begin{aligned}\langle \mathbf{A}_\mathrm{R}\mathbf{A}_\mathrm{R}^\mathrm{T}\rangle &= \langle[\mathbf{A}_\mathrm{M} - \langle \mathbf{A}_\mathrm{M}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle\langle \mathbf{A}_\mathrm{S}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle^{-1}\mathbf{A}_\mathrm{S}] \\ &\quad \times [\mathbf{A}_\mathrm{M} - \langle \mathbf{A}_\mathrm{M}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle\langle \mathbf{A}_\mathrm{S}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle^{-1}\mathbf{A}_\mathrm{S}]^\mathrm{T}\rangle \\ &= \langle \mathbf{A}_\mathrm{M}\mathbf{A}_\mathrm{M}^\mathrm{T}\rangle - [\langle \mathbf{A}_\mathrm{M}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle\langle \mathbf{A}_\mathrm{S}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle^{-1}]\langle \mathbf{A}_\mathrm{S}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle[\langle \mathbf{A}_\mathrm{M}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle\langle \mathbf{A}_\mathrm{S}\mathbf{A}_\mathrm{S}^\mathrm{T}\rangle^{-1}]^\mathrm{T}.\end{aligned} \tag{11}$$

The product $\langle A_S^{(1)} A_M^T \rangle$ may be expanded as

$$\langle A_S^{(1)} A_M^T \rangle = \langle A_S^{(1)} A_S^{(1)T} \rangle + (N-1)\langle A_S^{(1)} A_S^{(2)T} \rangle \tag{12}$$

$$\langle A_M A_S^T \rangle = \langle A_S^{(1)} A_S^{(1)T} \rangle + (N-1)\langle A_S^{(2)} A_S^{(1)T} \rangle, \tag{13}$$

where N is the number of molecules in the system. By definition we have

$$\langle A_M A_S^T \rangle = \langle \mathbf{A}_S^{(1)} \mathbf{A}_S^{(1)T} \rangle [1 + Nf]. \tag{14}$$

Similarly,

$$\langle A_M A_M^T \rangle = N \langle \mathbf{A}_S \mathbf{A}_S^T \rangle [1 + Nf],$$

so that

$$A_R = A_M - \mathbf{A}_S(1 + Nf), \tag{15}$$

$$\langle \mathbf{A}_R \mathbf{A}_R^T \rangle = N \langle \mathbf{A}_S \mathbf{A}_S^T \rangle (1 + Nf) - \langle \mathbf{A}_S \mathbf{A}_S^T \rangle (1 + Nf)(1 + Nf) \tag{16}$$

$$\doteqdot N \langle \mathbf{A}_S \mathbf{A}_S^T \rangle (1 + Nf) \tag{17}$$

because $N \doteqdot 10^{23}$, and because intermolecular forces are short ranged on a macroscopic scale so that $Nf \approx 1$. The off-diagonal elements $\langle \mathbf{A}_R \mathbf{A}_S^T \rangle$ and $\langle \mathbf{A}_S \mathbf{A}_R^T \rangle$ of the susceptibility matrix $(\boldsymbol{\chi})$ of $\mathbf{A}$ are zero, so that

$$\boldsymbol{\chi} = \begin{bmatrix} \langle \mathbf{A}_S \mathbf{A}_S^T \rangle & \mathbf{0} \\ \mathbf{0} & N \langle \mathbf{A}_S \mathbf{A}_S^T \rangle (1 + Nf) \end{bmatrix}. \tag{18}$$

We may now proceed to solve eq. (1) in the simplest Markov approximation where the effective liouvillian ϕ is a delta function. The vector $\mathbf{A}$ is governed by[1])

$$\dot{\mathbf{A}}(t) = \mathrm{i}\boldsymbol{\Omega} \cdot \mathbf{A}(t) - \boldsymbol{\Gamma} \cdot \mathbf{A}(t) + \mathbf{F}(t), \tag{19}$$

where

$$\boldsymbol{\Gamma} = \boldsymbol{\Lambda} \cdot \boldsymbol{\chi}^{-1}. \tag{20}$$

Define the matrices $\boldsymbol{\lambda}_{12}$ and $\boldsymbol{\lambda}_{11}$ by $\mathbf{g}_{12} = \boldsymbol{\lambda}_{12} \boldsymbol{\lambda}_{11}^{-1}$, then

$$\boldsymbol{\Lambda} = \begin{bmatrix} \boldsymbol{\lambda}_{11}; & N\boldsymbol{\lambda}_{11}(\mathbf{g}_{12} - \mathbf{j}) \\ N\boldsymbol{\lambda}_{11}(\mathbf{g}_{21} - \mathbf{f}); & \boldsymbol{\lambda}_{11} N (1 + N\mathbf{g}) \end{bmatrix}, \tag{21}$$

where we have assumed that $\mathbf{g}$ has elements of the order $1/N$, so that $(1 + Nf)^2$ is small compared with $N(1 + N\mathbf{g})$. The resonance term $\mathrm{i}\boldsymbol{\Omega} \cdot \mathbf{A}(t)$ is defined by

$$\langle \dot{\mathbf{A}}(0) \mathbf{A}^T(0) \rangle \langle \mathbf{A}(0) \mathbf{A}^T(0) \rangle^{-1} \mathbf{A}(t)$$

and since $\mathbf{A}_S$ and $\mathbf{A}_R$ are orthogonal, this is null. The dissipation matrix $\boldsymbol{\Gamma}$ and the column vector $\mathbf{A}$ of eq. (19) together yield expressions for correlation functions of interest. We have the relation

$$\begin{bmatrix}\langle \boldsymbol{A}_{\mathrm{S}}(t)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{S}}(0)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle^{-1};\langle \boldsymbol{A}_{\mathrm{S}}(t)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{R}}(0)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle^{-1}\\ \langle \boldsymbol{A}_{\mathrm{R}}(t)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{S}}(0)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle^{-1};\langle \boldsymbol{A}_{\mathrm{R}}(t)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{R}}(0)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle^{-1}\end{bmatrix}$$

$$= \mathscr{L}_{\mathrm{a}}^{-1}\begin{bmatrix}\mathbf{1}s+\boldsymbol{\Gamma}_{11} & \boldsymbol{\Gamma}_{12}\\ \boldsymbol{\Gamma}_{21} & \mathbf{1}s+\boldsymbol{\Gamma}_{22}\end{bmatrix}. \tag{22}$$

Therefore:

$$\langle \boldsymbol{A}_{\mathrm{S}}(t)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{S}}(0)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle^{-1}$$
$$= \mathscr{L}_{\mathrm{a}}^{-1}([\mathbf{1}s+\boldsymbol{\Gamma}_{22}][(\mathbf{1}s+\boldsymbol{\Gamma}_{11})(\mathbf{1}s+\boldsymbol{\Gamma}_{22})-\boldsymbol{\Gamma}_{12}\boldsymbol{\Gamma}_{21}]^{-1}); \tag{23}$$

$$\langle \boldsymbol{A}_{\mathrm{R}}(t)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{R}}(0)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle^{-1}$$
$$= \mathscr{L}_{\mathrm{a}}^{-1}([\mathbf{1}s+\boldsymbol{\Gamma}_{11}][(\mathbf{1}s+\boldsymbol{\Gamma}_{11})(\mathbf{1}s+\boldsymbol{\Gamma}_{22})-\boldsymbol{\Gamma}_{12}\boldsymbol{\Gamma}_{21}]^{-1}); \tag{24}$$

$$\langle \boldsymbol{A}_{\mathrm{S}}(t)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{R}}(0)\boldsymbol{A}_{\mathrm{R}}^{\mathrm{T}}(0)\rangle^{-1}$$
$$= \mathscr{L}_{\mathrm{a}}^{-1}(-\boldsymbol{\Gamma}_{12}[(\mathbf{1}s+\boldsymbol{\Gamma}_{11})(\mathbf{1}s+\boldsymbol{\Gamma}_{22})-\boldsymbol{\Gamma}_{12}\boldsymbol{\Gamma}_{21}]^{-1}); \tag{25}$$

$$\langle \boldsymbol{A}_{\mathrm{R}}(t)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{S}}(0)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle^{-1}$$
$$= \mathscr{L}_{\mathrm{a}}^{-1}(-\boldsymbol{\Gamma}_{21}[(\mathbf{1}s+\boldsymbol{\Gamma}_{11})(\mathbf{1}s+\boldsymbol{\Gamma}_{22})-\boldsymbol{\Gamma}_{12}\boldsymbol{\Gamma}_{21}]^{-1}); \tag{26}$$

which are matrix equations governing the single particle and multiparticle rototranslational correlation functions, and linking the two levels of motion. We may now focus our attention on the single-particle level or multiparticle level separately.

2.1. *Single-particle rototranslation*

We denote:

$$\langle \boldsymbol{A}_{\mathrm{S}}(t)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle \equiv \begin{bmatrix}\langle \boldsymbol{x}(t)\boldsymbol{x}^{\mathrm{T}}(0)\rangle & \langle \boldsymbol{x}(t)\boldsymbol{y}^{\mathrm{T}}(0)\rangle\\ \langle \boldsymbol{y}(t)\boldsymbol{x}^{\mathrm{T}}(0)\rangle & \langle \boldsymbol{y}(t)\boldsymbol{y}^{\mathrm{T}}(0)\rangle\end{bmatrix}, \tag{27}$$

where $\boldsymbol{x}$ and $\boldsymbol{y}$ are defined through the definition of the column vector $\boldsymbol{A}_{\mathrm{S}}(t)$ itself.

Evaluating eq. (23) we have

$$\langle \boldsymbol{x}(t)\boldsymbol{x}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{x}(0)\boldsymbol{x}^{\mathrm{T}}(0)\rangle = \mathscr{L}_{\mathrm{a}}^{-1}[(s+\Gamma_{22}^{(11)})E(s)/F(s)], \tag{28}$$

$$\langle \boldsymbol{x}(t)\boldsymbol{y}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{y}(0)\boldsymbol{y}^{\mathrm{T}}(0)\rangle = \mathscr{L}_{\mathrm{a}}^{-1}[-\Gamma_{22}^{(12)}B(s)/F(s)], \tag{29}$$

$$\langle \boldsymbol{y}(t)\boldsymbol{x}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{x}(0)\boldsymbol{x}^{\mathrm{T}}(0)\rangle = \mathscr{L}_{\mathrm{a}}^{-1}[-\Gamma_{22}^{(21)}D(s)/F(s)], \tag{30}$$

$$\langle \boldsymbol{y}(t)\boldsymbol{y}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{y}(0)\boldsymbol{y}^{\mathrm{T}}(0)\rangle = \mathscr{L}_{\mathrm{a}}^{-1}[(s+\Gamma_{22}^{(22)})A(s)/F(s)], \tag{31}$$

where

$$F(s) = A(s)E(s) - B(s)D(s). \tag{32}$$

In eqs. (28) to (32) we define the matrix elements (Γ) by

$$\Gamma_{ij}^{lm} = \begin{bmatrix}\Gamma_{ij}^{(11)} & \Gamma_{ij}^{(12)}\\ \Gamma_{ji}^{(21)} & \Gamma_{ij}^{(22)}\end{bmatrix}. \tag{33}$$

and

$$
\begin{aligned}
A(s) &= (s+\Gamma_{11}^{(11)})(s+\Gamma_{22}^{(11)})+\Gamma_{11}^{(12)}\Gamma_{22}^{(21)}-\Gamma_{12}^{(11)}\Gamma_{21}^{(11)}-\Gamma_{12}^{(12)}\Gamma_{21}^{(21)},\\
B(s) &= s(\Gamma_{22}^{(12)}+\Gamma_{11}^{(12)})+\Gamma_{22}^{(12)}\Gamma_{11}^{(11)}+\Gamma_{11}^{(12)}\Gamma_{22}^{(22)}-\Gamma_{12}^{(11)}\Gamma_{21}^{(12)}-\Gamma_{12}^{(12)}\Gamma_{21}^{(22)},\\
C(s) &= s(\Gamma_{11}^{(21)}+\Gamma_{22}^{(21)})+\Gamma_{11}^{(21)}\Gamma_{22}^{(11)}+\Gamma_{22}^{(21)}\Gamma_{11}^{(22)}-\Gamma_{12}^{(21)}\Gamma_{21}^{(11)}-\Gamma_{12}^{(22)}\Gamma_{21}^{(21)},\\
D(s) &= (s+\Gamma_{11}^{(22)})(s+\Gamma_{22}^{(22)})+\Gamma_{11}^{(21)}\Gamma_{22}^{(12)}-\Gamma_{12}^{(21)}\Gamma_{21}^{(12)}-\Gamma_{12}^{(22)}\Gamma_{21}^{(22)}.
\end{aligned}
$$

The Γ_{ij}^{lm} elements may now be considered from a physical standpoint, allowing us to decipher the eq. (28) (for the components of the momentum autocorrelation function), or eq. (31) (for the angular momentum autocorrelation function) in terms of static and dynamic pair correlations between distinct molecules and in terms of a rototranslational friction matrix of the Langevin type. We note the definition

$$
\begin{aligned}
\boldsymbol{\Gamma} &= \begin{bmatrix} \boldsymbol{\Gamma}_{11} & \boldsymbol{\Gamma}_{12} \\ \boldsymbol{\Gamma}_{21} & \boldsymbol{\Gamma}_{22} \end{bmatrix} = \boldsymbol{\Lambda}\cdot\boldsymbol{\chi}^{-1} \\
&= \boldsymbol{\lambda}_{11}\langle \mathbf{A}_S\mathbf{A}_S^{\mathrm{T}}\rangle^{-1}\begin{bmatrix} \mathbf{1}\ ; & (g_{12}-f)(\mathbf{1}+Nf)^{-1} \\ N(g_{21}-f); & (\mathbf{1}+Ng)(\mathbf{1}+Nf)^{-1} \end{bmatrix}.
\end{aligned} \tag{34}
$$

In general, therefore, all the elements Γ_{ij}^{lm} of the dissipation matrix may be expressed in terms of the two matrices g and f of dynamic and static correlations, respectively. It follows that the single and multiparticle correlation functions are also so defined. We now go on to consider the structures of g and f. The latter may be expanded as

$$
f = \begin{bmatrix} \langle x^{(2)}(0)x^{(1)}(0)^{\mathrm{T}}\rangle\langle x^{(1)}(0)x^{(1)}(0)^{\mathrm{T}}\rangle^{-1}; \langle x^{(2)}(0)y^{(1)}(0)^{\mathrm{T}}\rangle\langle y^{(1)}(0)y^{(1)}(0)^{\mathrm{T}}\rangle^{-1} \\ \langle y^{(2)}(0)x^{(1)}(0)^{\mathrm{T}}\rangle\langle x^{(1)}(0)x^{(1)}(0)^{\mathrm{T}}\rangle^{-1}; \langle y^{(2)}(0)y^{(1)}(0)^{\mathrm{T}}\rangle\langle y^{(1)}(0)y^{(1)}(0)^{\mathrm{T}}\rangle^{-1} \end{bmatrix}, \tag{35}
$$

where we have used the notation of eqs. (28) to (32). The elements f_{ij} measure the pair correlation between the vectors of momentum and angular momentum on molecules (1) and (2). Similarly g measures the dynamic correlations between a vector on molecule (2) at $t = 0$ and molecule (1) at t or vice-versa. If there is no pair correlation in the system at all, then both f and g are null. It is possible, therefore, to calculate the hydrodynamic and autocorrelation functions using only the static and dynamic pair correlations.

2.1.1. *Comparison with molecular dynamics simulations and spectra*

In principle, a mode–mode mixing theory such as the one outlined above may be rigorously tested with a computerised simulator. The method would consist of simulating the matrices f and g, various single and multiparticle correlation functions and using the analytical theory to link the results. Any remaining discrepancy between the simulated functions and analytical theory can be attributed to either:

(a) the need for non-Markovian statistics (section 3);
(b) coupling on the macroscopic level to other modes (see section 4).

To evaluate the theory with dielectric spectroscopy we recommend the following procedures:

(a) The far infrared portion of the spectrum should be regarded as an integral part of the loss process, so that the effect of inertia and memory in the equations of motion can be estimated.

(b) The problem of interacting dipoles (and the internal field adjustments[20]) can be minimised while keeping open the question of multiparticle, cooperative dynamics by choosing a mesophase of weakly dipolar molecules and monitoring the effect of dilution over the complete zero–THz range.

(c) The extent of rotation–translation coupling may be varied by measuring the spectra of liquid and plastic crystalline samples. In the latter case the centre of mass diffusion is very slow and there is of course a very high degree of positional correlation.

(d) The problem of many parameters may be tackled by using different spectral techniques and the simulator to investigate the same specimen.

2.1.2. *Relation of angular momentum and orientational autocorrelation functions*

In this paper we have adopted the overall strategy of applying Mori theory to the momentum and angular momentum vectors, since these determine the molecular motion via equation analogous to those of Langevin for the Brownian motion. In the light of these arguments we are left with the problem of relating the single molecule angular momentum autocorrelation function (or multiparticle correlation function as the case may be) to the function observed experimentally in dielectric spectroscopy and defined in eq. (1). In the simplest case of uncoupled, uncorrelated angular motion constrained to a plane, this problem has been treated in detail by McConnell and co-workers[21]). Suffice it to say that for angular motion of the asymmetric top dipole vector in a plane (rather than in 3-D space) there exists a relation between the angular velocity and orientational autocorrelation functions of the following kind[22]):

$$\langle u(t)\cdot u(0)\rangle = \exp\left[-\frac{kT}{I}\int_0^t (t-\tau)\langle\omega(\tau)\omega(0)\rangle \mathrm{d}\tau\right]. \tag{36}$$

Here u is the dipole unit vector, I the moment of inertia about the fixed lab. axis defining ω, the angular velocity component. Applying this constraint generally to the theory above means that the tranpose function appearing in eqs. (35), for example, could be replaced, when considering single molecule motion, by the relevant components. Removing the constraint of rotation in a plane introduces a considerable increase in complexity when dealing with relations such as eqs. (35) and (36). It is obvious in the general case that we must use numerical methods.

2.2. *Multiparticle correlation functions*

We denote:

$$\begin{aligned}\langle \mathbf{A}_\mathrm{R}(t)\mathbf{A}_\mathrm{R}^\mathrm{T}(0)\rangle &\equiv \begin{bmatrix}\langle \boldsymbol{X}(t)\boldsymbol{X}^\mathrm{T}(0)\rangle & \langle \boldsymbol{X}(t)\boldsymbol{Y}^\mathrm{T}(0)\rangle\\ \langle \boldsymbol{Y}(t)\boldsymbol{X}^\mathrm{T}(0)\rangle & \langle \boldsymbol{Y}(t)\boldsymbol{Y}^\mathrm{T}(0)\rangle\end{bmatrix}\\ &= \langle \mathbf{A}_\mathrm{M}(t)\mathbf{A}_\mathrm{M}^\mathrm{T}(0)\rangle \end{aligned} \tag{37}$$

to a good approximation. Evaluating eq. (24) gives a set of equations analogous to eqs. (28) to (32) with Γ_{22} elements replaced by Γ_{11} elements.

We note that in eqs. (23) to (26), if the following inequality is true:

$$\boldsymbol{\Gamma}_{12}\boldsymbol{\Gamma}_{21} \ll (\mathbf{1}s + \boldsymbol{\Gamma}_{11})(\mathbf{1}s + \boldsymbol{\Gamma}_{22}), \tag{38}$$

then the following generalisation of the macro–micro correlation theorem of Kivelson et al.^{23,24}) follows:

$$\langle \mathbf{A}_\mathrm{S}(t)\mathbf{A}_\mathrm{S}^\mathrm{T}(0)\rangle\langle \mathbf{A}_\mathrm{S}(0)\mathbf{A}_\mathrm{S}^\mathrm{T}(0)\rangle^{-1} = \mathscr{L}_\mathrm{a}^{-1}[(\mathbf{1}s + \boldsymbol{\Gamma}_{11})^{-1}]; \tag{39}$$

$$\langle \mathbf{A}_\mathrm{M}(t)\mathbf{A}_\mathrm{M}^\mathrm{T}(0)\rangle\langle \mathbf{A}_\mathrm{M}(0)\mathbf{A}_\mathrm{M}^\mathrm{T}(0)\rangle^{-1} = \mathscr{L}_\mathrm{a}^{-1}[(\mathbf{1}s + \boldsymbol{\Gamma}_{22})^{-1}]; \tag{40}$$

$$\langle \mathbf{A}_\mathrm{S}(t)\mathbf{A}_\mathrm{R}^\mathrm{T}(0)\rangle\langle \mathbf{A}_\mathrm{R}(0)\mathbf{A}_\mathrm{R}^\mathrm{T}(0)\rangle^{-1} = \mathscr{L}_\mathrm{a}^{-1}[-\boldsymbol{\Gamma}_{12}((\mathbf{1}s + \boldsymbol{\Gamma}_{11})(\mathbf{1}s + \boldsymbol{\Gamma}_{22}))^{-1}]; \tag{41}$$

$$\langle \mathbf{A}_\mathrm{R}(t)\mathbf{A}_\mathrm{S}^\mathrm{T}(0)\rangle\langle \mathbf{A}_\mathrm{S}(0)\mathbf{A}_\mathrm{S}^\mathrm{T}(0)\rangle^{-1} = \mathscr{L}_\mathrm{a}^{-1}[-\boldsymbol{\Gamma}_{21}((\mathbf{1}s + \boldsymbol{\Gamma}_{11})(\mathbf{1}s + \boldsymbol{\Gamma}_{22}))^{-1}]. \tag{42}$$

Formally, the correlation-time matrices of eqs. (39) and (40) are in the ratio

$$[\mathbf{1} + N\boldsymbol{f}][\mathbf{1} + N\boldsymbol{g}]^{-1}. \tag{43}$$

2.2.1. *The decoupled limit of 'pure rotation'*

In the decoupled limit the vectors $\mathbf{A}_\mathrm{S}$ and $\mathbf{A}_\mathrm{M}$ reduce to one component columns. In the Markov approximation to eq. (1) the correlation matrices $\boldsymbol{g}$ and $\boldsymbol{f}$ reduce to scalars and the correlation times of $\mathbf{A}_\mathrm{S}$ and $\mathbf{A}_\mathrm{M}$ are in the ratio of eq. (43). However, it is well-known from the results of far infrared spectroscopy^{10}) that the Markov approximation is over-simplistic in the case of uncoupled rotation and that a continued-fraction expansion of eq. (1) is necessary. We develop the formalism for the vector $\mathbf{A} = \begin{bmatrix}\mathbf{A}_\mathrm{S}\\ \mathbf{A}_\mathrm{M}\end{bmatrix}$ in section 3. This provides a substructure for the general rototranslational theory that follows. For uncoupled rotation, and also in general, $\mathbf{A}$ obeys a diffusion equation derived by Davies and Evans^{25}) which governs the behaviour of the associated probability density function $p(\mathbf{A}, \mathbf{A}(0)|\, t)$. It is therefore possible to write down a great deal of information about the nature of the effect of distinct static and dynamic pair correlations on the variance of the molecular angular velocity and spin density. By constraining the motion of the dipole moment to a plane it is possible to use eq. (36) to link the final expression for the autocorrelation function of angular velocity, for example, to the zero–THz power absorption spectrum. In section 2, we develop eq. (1) into a multi-dimensional chain of Markov equations, the last of which having the structure of eq. (19). The number of equations in this chain is determined by the approximant taken for the infinite continued fraction representation of eq. (1).

3. Generalisation to non-Markovian statistics

It has been shown elsewhere$^{14-16}$) that eq. (1) is fully equivalent to the Markov chain

$$\frac{\mathrm{d}}{\mathrm{d}t}\boldsymbol{V} = \mathrm{i}\boldsymbol{\omega}\cdot\boldsymbol{V} - \boldsymbol{\alpha}\cdot\boldsymbol{V} - \boldsymbol{\sigma}\cdot\boldsymbol{V} + \boldsymbol{\Phi}(t). \tag{44}$$

Here $\boldsymbol{V}$ is a grand column vector of n dynamical variables $\boldsymbol{B}$ which are, in turn, mth dimensional vectors. So we have the series of linked equations defined by the structure of the resonance matrix $\boldsymbol{\omega}$, the random force vector $\boldsymbol{\Phi}(t)$, the dissipation matrix $\boldsymbol{\sigma}$ and the 'virtual variable' matrix $\boldsymbol{\alpha}$. If the resonance matrix is null, then

$$\begin{aligned}
\dot{\boldsymbol{B}}_1 &= -\boldsymbol{\alpha}_{12}\boldsymbol{B}_2 - \boldsymbol{\gamma}\boldsymbol{B}_1 + \boldsymbol{F}(t),\\
\dot{\boldsymbol{B}}_2 &= -\boldsymbol{\alpha}_{21}\boldsymbol{B}_1 - \boldsymbol{\alpha}_{23}\boldsymbol{B}_3,\\
\dot{\boldsymbol{B}}_3 &= -\boldsymbol{\alpha}_{32}\boldsymbol{B}_2 - \boldsymbol{\alpha}_{34}\boldsymbol{B}_4,\\
&\ \ \vdots\\
\boldsymbol{B}_{n+1} &= \dot{\boldsymbol{0}}.
\end{aligned} \tag{45}$$

By using various n in eqs. (45) it is possible to build up a non-Markovian set of macro–micro correlation theorems linking the angular momentum and spin density correlation functions. We note that the set of equations represented by (44) is tractable for the space rotation of the asymmetric top whereas eq. (1) is not. When $n = 1$ eqs. (45) must reduce to eq. (19) (with a null resonance operator). We therefore see that we may use in eq. (45) a form for $\boldsymbol{\gamma}$, the dissipation matrix, analogous to that of in eq. (19). It follows that:

$$\boldsymbol{\gamma} = \begin{bmatrix} \gamma_{SS} & \gamma_{SR} \\ \gamma_{RS} & \gamma_{RR} \end{bmatrix} = L_{11}\begin{bmatrix} 1 & N(\hat{g}_{12} - \hat{f}) \\ N(\hat{g}_{21} - \hat{f}) & N(1 + N\hat{g}) \end{bmatrix}, \tag{46}$$

where $\hat{g}$ and $\hat{f}$ are dynamic and static pair correlation factors of the angular momentum of distinct molecules. L_{11} is a factor analogous to λ_{11} of eq. (21). $\hat{g}$ and $\hat{f}$ relate the correlation times of the nth memory function of the column vector of $\mathbf{A}_S$ and $\mathbf{A}_R$, through an equation such as (43). The matrices $\boldsymbol{\alpha}_{ij}$ are all diagonal because $\mathbf{A}_S$ and $\mathbf{A}_R$ are orthogonal by definition. If we embed a dipole vector in the asymmetric top and constrain the libration of the dipole to a plane it is possible to obtain from the system (45) closed solutions for the autocorrelation function of (scalar) angular velocity and spin density. In the dielectric limit of $\mathbf{k}\rightarrow\mathbf{0}$, and choosing, for example, $n = 3$ (itinerant libration) we obtain the results

$$\mathscr{L}_{\mathrm{a}}\left[\frac{\langle\omega_1(t)\omega_1(0)\rangle}{\langle\omega_1(0)\omega_1(0)\rangle}\right] = \xi_1(s)/\xi_2(s), \tag{47}$$

$$\mathscr{L}_{\mathrm{a}}\left[\frac{\left\langle\sum_{i=1}^{N}\omega_i(t)\sum_{i=1}^{N}\omega_i(0)\right\rangle}{\left\langle\sum_{i=1}^{N}\omega_1(0)\sum_{i=1}^{N}\omega_i(0)\right\rangle}\right] \doteqdot \mathscr{L}_{\mathrm{a}}[\langle\mathbf{A}_{\mathrm{R}}(t)\cdot\mathbf{A}_{\mathrm{R}}(0)\rangle\langle\mathbf{A}_{\mathrm{R}}(0)\cdot\mathbf{A}_{\mathrm{R}}(0)\rangle^{-1}]$$

$$= \xi_3(s)/\xi_2(s). \tag{48}$$

In eqs. (47) and (48),

$$\begin{aligned}\xi_2(s) = {} & (s^2+\Delta_2^{(S)2})(s^2+\Delta_2^{(R)2})((s+\gamma_{SS})(s+\gamma_{RR})-\gamma_{RS}\gamma_{SR})\\ & + s((s+\gamma_{SS})\Delta_2^{(S)2}\Delta_1^{(R)2}+(s+\gamma_{RR})\Delta_1^{(S)2}\Delta_2^{(R)2})\\ & + s^3(\Delta_1^{(R)2}(s+\gamma_{SS})+\Delta_1^{(S)2}(s+\gamma_{RR}));\end{aligned} \tag{49}$$

$$\begin{aligned}\xi_1(s) = {} & s(s^2+\Delta_2^{(R)2})[(s+\gamma_{SS})(s+\gamma_{RR})-\gamma_{RS}\gamma_{SR}]\\ & + s^2[\Delta_1^{(S)2}(s+\gamma_{RR})+\Delta_1^{(R)2}(s+\gamma_{SS})]\\ & + \Delta_1^{(S)2}(s\Delta_1^{(R)2}+(s+\gamma_{RR})\Delta_2^{(R)2});\end{aligned} \tag{50}$$

$$\begin{aligned}\xi_3(s) = {} & s(s^2+\Delta_2^{(S)2})[(s+\gamma_{RR})(s+\gamma_{SS})-\gamma_{RS}\gamma_{SR}]\\ & + s^2[\Delta_1^{(R)2}(s+\gamma_{SS})+\Delta_1^{(S)2}(s+\gamma_{RR})]\\ & + \Delta_1^{(R)2}(s\Delta_1^{(S)2}+(s+\gamma_{SS})\Delta_2^{(S)2}).\end{aligned} \tag{51}$$

The equilibrium averages $\Delta_1^{(R)}$, $\Delta_2^{(R)}$, $\Delta_1^{(S)}$ and $\Delta_2^{(S)}$ are defined as follows:

$$\Delta_2^{(S)2} = \langle\dot{\mathbf{A}}_S^2(0)\rangle/\langle\mathbf{A}_S^2(0)\rangle;\Delta_2^{(R)2} = \langle\dot{\mathbf{A}}_R^2(0)\rangle/\langle\mathbf{A}_R^2(0)\rangle;$$

$$\Delta_1^{(S)2} = \frac{\langle\ddot{\mathbf{A}}_S^2(0)\rangle}{\langle\dot{\mathbf{A}}_S^2(0)\rangle} - \frac{\langle\dot{\mathbf{A}}_S^2(0)\rangle}{\langle\mathbf{A}_S^2(0)\rangle};\Delta_1^{(R)2} = \frac{\langle\ddot{\mathbf{A}}_R^2(0)\rangle}{\langle\dot{\mathbf{A}}_R(0)\rangle} - \frac{\langle\dot{\mathbf{A}}_R(0)\rangle}{\langle\mathbf{A}_R(0)\rangle}.$$

In the case where there is no intermolecular correlation in the system we have $\Delta_1^{(R)2} = \Delta_2^{(R)2} = 0$ and $\gamma_{RS}\gamma_{SR} = 0$ so that eq. (47) reduces to the well-known result for single molecule planar libration:

$$\frac{\mathscr{L}_{\mathrm{a}}[\langle\omega_1(t)\omega_1(0)\rangle]}{\langle\omega_1(0)\omega_1(0)\rangle} = \frac{s^2+\gamma_{SS}s+\Delta_1^{(S)2}}{s^3+\gamma_{SS}s^2+(\Delta_1^{(S)2}+\Delta_2^{(S)2})s+\Delta_2^{(S)2}\gamma_{SS}}. \tag{52}$$

The result, eq. (52), is helpful in attempting to explain the physical meaning of the dissipation matrix γ, because we may identify γ_{SS} of eq. (52) with the equivalent term obtainable by direct solution of the itinerant librator equations of motion. This is the frequency at which the inner molecule is bound harmonically to the outer cage, which as a rigid entity, is undergoing Brownian motion. By intuitive analogy therefore γ_{RR} is a frequency connected with this kind of motion on the multiparticle scale. This latter is not, however, a vortex type of motion since the vortex is generated only by a full consideration of translation of the molecular centres of mass. It is rather a phenomenon of collective spins.

3.1. *Comparison of eqs.* (47) *and* (48) *with experimental data*

The state of the art is at a point where it is becoming more difficult to compare effectively the formalism and spectra. Equations (47) and (48) involve seven variables which we can regard as phenomenological. It is necessary to obtain a broad-range of results to evaluate each individually. The increasing use of molecular dynamics simulation is easing the difficulty considerably, however, because it is possible to construct on the computer any molecular dynamical property whose variance or covariance is known analytically. If the analytical approximation is written in terms of seven parameters, then these can be estimated using seven (or many more) different simulated averages. In addition the theory has to be able to describe in a consistent manner a variety of spectra, of which the zero–THz power absorption is one incisive example, and depolarised Rayleigh scattering another. Also, it is known that some techniques pick up information about single-particle motion only (e.g. NMR relaxation), which is helpful.

It is clear that the zero–THz spectrum alone can be used to estimate all seven variables by using a multiparameter, non-linear iteration algorithm; but, as we shall see in section 4, the power absorption coefficient ($\alpha(\omega)$) over this very broad frequency range contains in theory information about mode–mode coupling (of the hydrodynamic type) as $\boldsymbol{k} \to \boldsymbol{0}$ is approached. Dividing $\alpha(\omega)$ by ω^2 produces the equivalent of the observable intensity in a depolarised light scattering experiment, and no doubt it is possible to reproduce in this way the equivalent of the well-known Rytov splitting[1]). By an unfortunate historical accident the Cole–Cole plot is often still used in analysing dielectric data. Not only is this the least discriminating method of data evaluation imaginable, but also the all-important far infra-red contribution is often ignored experimentally.

3.2. *Non-Markovian theory of rototranslation and pair correlation*

This is the case where eq. (1) must be solved without early approximation subject to the definitions in eqs. (7) and (6). The numerical and multidimensional (eq. (45)) methods of Grigolini and coworkers[14–16]) are particularly useful for this problem because they provide a link with the highly developed basis set and diagonalisation methods of quantum perturbation theory.

Having dealt with the problem of pair correlation with spin and current density we consider in section 4 the additional roles of the particle and energy density when these are coupled in a Mori framework to the single molecule angular momentum.

4. Discussion

In this section we aim to use the results of hydrodynamics to simplify and give physical meaning to equations such as (37). Berne and coworkers[17]) have shown that the angular momentum of an individual molecule couples to the transverse component of the *linear* momentum field vector. If a molecule is set in rotational motion in an otherwise stationary fluid it will slow down by creating a vortex field (transverse) around itself. This introduces a very long time tail into the decay of the molecular angular momentum autocorrelation function[26]). This is kinematically related to the dipole autocorrelation function observable in a dielectric experiment. We note that it is possible to derive the same result in principle by constructing a macro–micro correlation between the vector: $\mathbf{A}_{\mathrm{M}} = \begin{bmatrix} g_x \\ S_y \end{bmatrix}$ and its single particle equivalent. Here g_x and S_y are as defined in section 2. We note that the $t^{-5/2}$ dependence predicted at long times in the angular momentum autocorrelation function is arrived at by integrating out the dependence of $\langle S_y(t) S_y(0) \rangle$ on position, i.e. by integrating $\langle S_y(r, t) S_y(0, 0) \rangle$ over the volume of the original fluid element, which is assumed not to have moved from its original position $(r = 0)_0$. If there is finite rotation–translation coupling on the molecular scale this assumption is in a strict sense invalidated. Another subtle point is that an essential step in the derivation of the $t^{-5/2}$ dependence is the long-time relation

$$S_y(k, t) = -\frac{ik}{m\rho} g_x(k, t), \tag{53}$$

where ρ is the number density and m the mass. If we take the view that a dielectric experiment is a measurement with $\mathbf{k} = \mathbf{0}$, then the left hand side of eq. (53) vanishes. We cannot construct an angular momentum autocorrelation function by this means. Rather we must keep k infinitesimal but *finite* and integrate for the final result at the correct stage in the calculation. This is equivalent to saying that in a dielectric experiment we are observing translation only indirectly, via the rotatory motions only. There is a k-dependence, but there is no *observable* k-dependence. There is a mutual effect of translation and rotation, but only the rotation is *observable.*

Our eq. (39) effectively measures (among other things) the effect of vorticity on the zero–THz power absorption coefficient. However, the form of eq. (39) is complicated and to clarify the underlying physical significance we proceed as follows. Because the total spin density is invariant under parity transformation only S_y and g_x are correlated. Berne et al.[17]) have shown that transverse correlation matrix $C^{\mathrm{t}}(k, z)$ is given from eq. (1) by

$$C^{\mathrm{t}}(k, z) = \frac{1}{\mathrm{i}} C^{\mathrm{t}}(k, 0)[z - \mathrm{i}K^{\mathrm{t}}(k, z)]^{-1}, \tag{54}$$

where

$$K^{\mathrm{t}}(k, z) = \begin{bmatrix} k^2[\eta(z) + \eta_{\mathrm{r}}(z)]/m\rho\,; -2\mathrm{i}k\eta_{\mathrm{r}}(z)/I\rho \\ 2\mathrm{i}k\eta_{\mathrm{r}}(z)/m\rho\,; 4\eta_{\mathrm{r}}(z)/I\rho + k^2 D_{\mathrm{t}} \end{bmatrix}.$$

Here $\mathrm{i}z \equiv s$, η is the frequency dependent shear viscosity, η_{r} the frequency dependent rotational viscosity, I the *average* moment of inertia of the general asymmetric top. We have

$$\eta(z) = \lim_{k\to 0}\left[\frac{\rho}{k_{\mathrm{B}}T}\int_0^\infty \mathrm{d}t\; \mathrm{e}^{-\mathrm{i}zt}\langle \tau^{\mathrm{s}*}_{xz}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\tau^{\mathrm{s}}_{xz}(k)\rangle\right], \tag{55}$$

$$D_{\mathrm{t}}(z) = \lim_{k\to 0}\left[(Ik_{\mathrm{B}}T)^{-1}\int_0^\infty \mathrm{d}t\; \mathrm{e}^{-\mathrm{i}zt}\langle \sigma^{*}_{xz}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\sigma_{xz}(k)\rangle\right], \tag{56}$$

$$\eta_{\mathrm{r}}(z) = \lim_{k\to 0}\left[\frac{\rho}{k_{\mathrm{B}}T}\int_0^\infty \mathrm{d}t\; \mathrm{e}^{-\mathrm{i}zt}\langle \tau^{\mathrm{a}*}_{xz}(k)\mathrm{e}^{\mathrm{i}(-P)\mathscr{L}t}(1-P)\tau^{\mathrm{a}}_{xz}(k)\rangle\right], \tag{57}$$

where τ^{a}_{ij} is the antisymmetric part of the *microscopic* stress tensor defined by $\tau^{\mathrm{a}}_{ij} = \frac{1}{2}(\tau_{ij} - \tau_{ji})$. This is a torque density which couples rotational and translational motion. If $\tau^{\mathrm{a}}_{ij} = 0$ the spin density is independently conserved and *the intermolecular forces are purely central.* σ_{ij} is the spin current defined by the relation

$$\frac{\partial}{\partial t}S_i(r, t) + \nabla_j\sigma_{ij}(r, t) = \epsilon_{ijk}\tau^{\mathrm{a}}_{ij}(r, t), \tag{58}$$

where ϵ_{ijk} is the Levi-Civita symbol. Equation (54) refers to the limit of small k where k^3 terms are negligible. Taking the limit $k \to 0$ is equivalent to performing the integration

$$\int \mathrm{d}r\,\tau^{\mathrm{a}}_{ij}(r) = -\frac{1}{4}\epsilon_{ijk}\sum_{\alpha\neq\beta}[(r^{\alpha} - r^{\beta})\times F^{\alpha\beta}], \tag{59}$$

where $F^{\alpha\beta}$ is the force between molecules α and β. Equation (59) illustrates how a torque may be imparted on a multi or single-molecule level by a translational force. On a single particle level the integral in eq. (59) is closely analogous to the rototranslational Langevin friction term, being inter alia existent or non-existent as the case may be.

In the absence of pair correlation ($f = g = 0$ in eq. (39)) we may make the following identities, and also define the single-particle momentum and angular momentum autocorrelation functions in terms of hydrodynamic quantities:

$$\Gamma_{22}^{11} = k^2(\eta(s) + \eta_{\mathrm{r}}(s))/m\rho; \tag{60}$$

$$\Gamma_{22}^{12} = -2\mathrm{i}k\eta_{\mathrm{r}}(s)/I\rho; \tag{61}$$

$$\Gamma_{22}^{21} = 2\mathrm{i}k\eta_{\mathrm{r}}(s)/m\rho; \tag{62}$$

$$\Gamma_{22}^{22} = 4\eta_{\mathrm{r}}(s)/I\rho + k^2D_{\mathrm{t}}. \tag{63}$$

Noting that when $\mathbf{g} = f = \mathbf{0}$

$$\langle \boldsymbol{A}_{\mathrm{S}}(t)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle = N^{-1}\langle \boldsymbol{A}_{\mathrm{M}}(t)\boldsymbol{A}_{\mathrm{M}}^{\mathrm{T}}(0)\rangle \tag{64}$$

then eqs. (60) to (63) also define the nature of the single particle rototranslational autocorrelation matrix. In the case where the rotating and translating body is structureless but endowed with spin, we may write:

$$\mathscr{L}_{\mathrm{a}}[\langle \boldsymbol{A}_{\mathrm{S}}(t)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle\langle \boldsymbol{A}_{\mathrm{S}}(0)\boldsymbol{A}_{\mathrm{S}}^{\mathrm{T}}(0)\rangle^{-1}] = \begin{bmatrix} s + \gamma_{\mathrm{t}}(s) & \gamma_{\mathrm{tr}}(s) \\ \gamma_{\mathrm{rt}}(s) & s + \gamma_{\mathrm{r}}(s) \end{bmatrix}^{-1} \tag{65}$$

in the hydrodynamic limit. Here the γ's are hydrodynamic friction coefficients which may be frequency dependent if the governing statistics are not Markovian. Note that eq. (65) is the solution to the rototranslational single-particle Langevin equation:

$$m\dot{\boldsymbol{v}} = -m\gamma_{\mathrm{t}}\boldsymbol{v} - \gamma_{\mathrm{tr}}I\boldsymbol{\omega} + \boldsymbol{F}, \tag{66}$$

$$I\dot{\boldsymbol{\omega}} = -I\gamma_{\mathrm{r}}\boldsymbol{\omega} - \gamma_{\mathrm{rt}}m\boldsymbol{v} + \boldsymbol{T}, \tag{67}$$

if the γ's are frequency independent. Using eqs. (60) to (65) we have, in the hydrodynamic limit;

$$\gamma_{\mathrm{t}}(s) = \lim_{k\to 0}\left[\frac{k^2}{mk_{\mathrm{B}}T}\left[\int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st}\langle \tau_{xz}^{\mathrm{s}*}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\tau_{xz}^{\mathrm{s}}(k)\rangle\right.\right.$$
$$\left.\left. + \int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st}\langle \tau_{xz}^{\mathrm{a}*}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\tau_{xz}^{\mathrm{a}}(k)\rangle\right]\right], \tag{68}$$

$$\gamma_{\mathrm{tr}}(s) = \lim_{k\to 0}\left[-\frac{2\mathrm{i}k}{k_{\mathrm{B}}TI}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st}\langle \tau_{xz}^{\mathrm{a}*}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\tau_{xz}^{\mathrm{a}}(k)\rangle\right]; \tag{69}$$

$$\gamma_{\mathrm{rt}}(s) = \lim_{k\to 0}\left[\frac{2\mathrm{i}k}{k_{\mathrm{B}}Tm}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st}\langle\tau_{xz}^{\mathrm{a}*}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\tau_{xz}^{\mathrm{a}}(k)\rangle\right]; \tag{70}$$

$$\gamma_{\mathrm{r}}(s) = \lim_{k\to 0}\left[\frac{4}{k_{\mathrm{B}}TI}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st}\langle\tau_{xz}^{\mathrm{a}*}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\tau_{xz}^{\mathrm{a}}(k)\rangle\right.$$

$$\left.+\frac{k^2}{Ik_{\mathrm{B}}T}\int_0^\infty \mathrm{d}t\ \mathrm{e}^{-st}\langle\sigma_{xz}^{*}(k)\mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t}(1-P)\sigma_{xz}(k)\rangle\right]. \tag{71}$$

Equations (69) to (71) demonstrate that:

(a) when the forces between molecules are purely central there is no rotation translation coupling because the antisymmetric part of the microscopic stress tensor vanishes;

(b) when there is a finite rotation translation coupling the friction coefficients $\gamma_{\mathrm{t}}(s)$ and $\gamma_{\mathrm{r}}(s)$ contain information on the antisymmetric part of the microscopic stress tensor.

When the frequency dependence of the γ's in eqs. (68) to (71) vanishes, Berne et al. have shown that their structure is unchanged at long times. When there is long-range order in the system g and f remain finite, and the parity rules leading to transverse coupling only also break down. There is therefore in liquid crystals the possibility of longitudinal as well as transverse coupling between spin and current density. This is already accounted for in the formalism of section 2 but through the intermediacy of many parameters Γ_{ij}^{lm}. Obviously the many-particle mode–mode interactions are reflected, through g and f, in the single particle autocorrelation functions and therefore in the zero–THz spectra. However, it is possible to conclude from eqs. (68) to (71) that the highly anisotropic potential in liquid crystalline molecules will favour a strong rotation–translation interaction via a pronouncedly asymmetric stress tensor.

4.1. *Finite pair correlation*

In this case the matrices g and f are finite and we have

$$\langle A_{\mathrm{M}}(s)A_{\mathrm{M}}^{\mathrm{T}}(0)\rangle\langle A_{\mathrm{S}}(s)A_{\mathrm{S}}^{\mathrm{T}}(0)\rangle^{-1}$$
$$= N(1+Nf)[1s+\Gamma_{22}(1+Ng)(1+Nf)^{-1}]^{-1} \tag{72}$$

and

$$\langle A_{\mathrm{M}}(s)A_{\mathrm{M}}^{\mathrm{T}}(0)\rangle\langle A_{\mathrm{S}}(s)A_{\mathrm{S}}^{\mathrm{T}}(0)\rangle^{-1} = [1s+\Gamma_{22}]^{-1}. \tag{73}$$

The elements of Γ_{22} are identified hydrodynamically in this case through the matrix equation

$$\Gamma_{22}(\mathbb{1} + Ng)(\mathbb{1} + Nf)^{-1} = \boldsymbol{\theta}, \tag{74}$$

where the elements of $\boldsymbol{\theta}$ are defined by eqs. (60) to (63).

4.2. *Longitudinal coupling-Angular momentum and spin density*

In section 3 we have treated this problem in general terms, but when the spin density component is taken parallel to $\boldsymbol{k}$ (along the laboratory z-axis). In this case the so-called longitudinal spin density is decoupled from all other modes. Its first memory function is:

$$K_s(k, s) = \frac{1}{Ik_B T} \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st} \langle \dot{S}_z^*(k) \mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t} (1-P) \dot{S}_z(k) \rangle \tag{75}$$

with

$$\dot{S}_z(k) = \mathrm{i}k\sigma_{zz}(k) + 2\lambda \hat{\tau}^{\mathrm{a}}_{xy}(k). \tag{76}$$

We define, following Berne et al., $\tau^{\mathrm{a}}_{ij} = \lambda \hat{\tau}^{\mathrm{a}}_{ij}$ for the antisymmetric part of the microscopic stress tensor where λ is the strength of the interparticle torque. It is useful to construct a macro–micro correlation theorem between $S_z(k, t)$ and the molecular angular momentum autocorrelation function. This serves to illuminate the fact that the microscopic rotational friction coefficient of dielectric and light scattering theory contains implicitly information on the *linear* velocity (or momentum) correlation time through the intermediacy of the spin diffusion coefficient D, defined by

$$D = (Ik_B T)^{-1} \lim_{\epsilon \to 0} \lim_{\substack{k \to 0 \\ \lambda \to 0}} \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\epsilon t} \langle \sigma^*_{zz}(k) \mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t} (1-P) \sigma_{zz}(k) \rangle. \tag{77}$$

Consider now the two component vector defined by: $A_M = S_z$ and the second element of eq. (2). Performing the calculation of section 2 leads to the following relation when the factors g and f vanish (in the absence of pair correlation):

$$\lim_{k \to 0} \left[(Ik_B T)^{-1} \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-st} \langle \dot{S}_z^*(k) \mathrm{e}^{\mathrm{i}(1-P)\mathscr{L}t} (1-P) \dot{S}_z(k) \rangle \right] = \gamma_r(s). \tag{78}$$

Comparing eqs. (78) and (71), through the intermediacy of eq. (76) we obtain a result similar to that of Lobo et al.27) who have proposed the existence of longitudinal and transverse plasmons which ought to be observable in a dipolar liquid by dielectric spectroscopy. This is because the rotational coefficient $\gamma_r(s)$ (the single particle angular momentum autocorrelation function) contains information about *both* the transverse and longitudinal spin densities (eqs. (71) and (78)). In the case where $\gamma_r(s)$ is frequency independent, eq. (77) reduces to

$$D = \lim_{\epsilon \to 0} \frac{1}{3} \int_0^\infty \mathrm{d}t\, \mathrm{e}^{-\epsilon t} \langle v(t) \cdot v(t) \rangle_{\lambda \to 0}, \tag{79}$$

i.e. the self-diffusion coefficient of centres of mass. In this case γ_r contains information on linear motion even when the formal coupling of rotation and translation is not considered.

5. The micro–macro correlation theorem

In this section we aim to show that without a micro–macro correlation theorem the interpretation of single molecule (autocorrelation function) theories in terms of hydrodynamic concepts runs into difficulties. For instance a Mori three variable theory applied to the molecular centre of mass linear velocity may be interpreted mechanically by the motion of a harmonically encaged particle, known as the itinerant oscillator (from the fact that the cage is itself assumed to be a diffusing entity). According to this model it is possible to express the velocity autocorrelation function $C(t)$ in the following exact form (that of eq. (52) effectively):

$$C(t) = \frac{\langle v(t) \cdot v(0) \rangle}{\langle v(0) \cdot v(0) \rangle} = \frac{2}{\pi} \int_0^\infty \mathrm{d}\omega \left[\frac{1}{-\mathrm{i}\omega + \cfrac{\Delta_1^2}{-\mathrm{i}\omega + \cfrac{\Delta_2^2}{-\mathrm{i}\omega + \hat{\xi}_M(\omega)}}} \right] \cos\omega t, \tag{80}$$

where $v(t)$ is the velocity and $\hat{\xi}(\omega)$ is defined by the following mechanical analogy:

$$\dot{v} = \ddot{x} = -\frac{K}{m}(x - y), \tag{81}$$

$$\dot{w} = \ddot{y} = \frac{K}{M}(x - y) - \int_0^t \xi_M(t - \tau) w(\tau) \mathrm{d}\tau. \tag{82}$$

with

$$\Delta_1^2 = K/m, \quad \Delta_2^2 = K/M;$$

$$\xi(t) = \mathscr{L}_{\mathrm{a}}^{-1}(\hat{\xi}(\omega)).$$

The mass of the encaged particle is m; x and y are coordinates of the system, fully defined elsewhere[22]). Since the mass m is not associated with any direct dissipation process it may be regarded as a particle inside a cage which may be represented by the mass M (of a 'virtual' body). However, if the radius R

of the 'virtual' body is equal or smaller than that of the real particle m, this mechanical picture cannot be accepted. The problem of finding $\hat{\xi}_M(\omega)$ analytically is very complicated but may be tackled, let us suppose, hydrodynamically. This is valid at long times where the simulations of Alder et al.[28]) may be reproduced as long tail in the autocorrelation function, decaying as $t^{-3/2}$.

The low frequency limiting behaviour in this case may be represented by:

$$C(t \to \infty) \doteqdot \frac{2}{\pi} \int_0^\infty \mathrm{d}\omega \frac{\Delta_2^2}{\Delta_1^2 \hat{\xi}_M(\omega)} \tag{83}$$

$$\doteqdot \frac{2}{\pi} \int_0^\infty \mathrm{d}\omega \frac{\Delta_2^2}{\Delta_1^2 (b + a\omega^{1/2})}, \tag{84}$$

so that mathematically $C(t) \to t^{-3/2}$. Physically, in our present context the external cage (or 'virtual' mass m) should behave in this manner according to hydrodynamics. At very long times the inner particle will move with the same velocity as the external cage, because of thermodynamic equilibrium. At intermediate times a complicated grey region must be investigated where hydrodynamic and molecular theories interrelate (section 4). The movement of the rigid body of mass m sets up vortices. The interaction of vortex and centre of mass velocity results in the $t^{-3/2}$ law.

Bixon and Zwanzig[29]) and Freed, Oxtoby et al.[30]) used for their hydrodynamic approach the relation

$$C(t) = \frac{2}{\pi} \int_0^\infty \mathrm{d}\omega \left[\frac{1}{-\mathrm{i}\omega + \hat{\xi}_{\mathrm{BZ}}(\omega)} \right] \cos \omega t, \tag{85}$$

where

$$\hat{\xi}_{\mathrm{BZ}} = \frac{4\pi a}{m} f(a, \eta_s^0, \eta_t^0, \tau_s, \tau_t, \rho_0, \omega)$$

Here η_s^0 is the zero-frequency shear viscosity, η_t^0 the zero-frequency longitudinal viscosity, τ_t the longitudinal relaxation time and τ_s the shear relaxation time. The parameters R and M are the only ones specific to the rigid body, whereas the remaining ones have to be related to the nature of the surrounding fluid. In the generalised hydrodynamics used by these authors the liquid is viscoelastic so that η_s and η_t become frequency dependent.

$$\eta_s = \eta_s^0 (1 - \omega \tau_s)^{-1},$$
$$\eta_t = \eta_t^0 (1 - \omega \tau_t)^{-1}. \tag{86}$$

These modifications are required to reproduce the essential features of

Rahman's computer simulation[31]) of the velocity a.c.f. of liquid argon. However, in this simple model the oscillation frequency ω_f, associated with the power spectrum of $\langle \boldsymbol{v}(t)\cdot\boldsymbol{v}(0)\rangle$, is more intense in the simulation than predicted by the model.

To improve the agreement we might attempt to extend the continued fraction in eq. (85) by taking the 'virtual' particle as a sphere of mass M and radius R. The hydrodynamic approach then implies taking in eq. (80):

$$\hat{\xi}_M(\omega) = \frac{4\pi R}{M} f(R, \eta_s^0, \eta_t^0, \tau_s, \tau_t, \rho_0, \omega). \tag{87}$$

It is then evident that, especially at very low frequencies, the following equality must be satisfied:

$$\hat{\xi}_{BZ}(\omega) = \cfrac{\Delta_1^2}{-i\omega + \cfrac{\Delta_2^2}{-i\omega + \hat{\xi}_M(\omega)}}. \tag{88}$$

At zero-frequency, eq. (88) implies that

$$\hat{\xi}_{BZ}(0) = \frac{\Delta_1^2}{\Delta_2^2}\hat{\xi}_M(0) = \frac{M}{m}\hat{\xi}_M(0) \tag{89}$$

and

$$4\pi a f(a, \eta_s^0, \eta_t^0, \tau_s, \tau_t, \rho_0, 0) = 4\pi R f(a, \eta_s^0, \eta_t^0, \tau_s, \tau_t, \rho_0, 0). \tag{90}$$

This means that the radius of the body endowed with mass M must be the same as the radius of the body m. Accordingly the concept of itinerant oscillation cannot easily be exploited in order to introduce hydrodynamics in the context of the Mori theory. It is evident that for translational relaxation evaluated using a hydrodynamic formalism the 'cage' must be replaced by a 'virtual' mass M. Alternatively, using thermodynamics and statistical ideas the external cage could be regarded as a thermal bath or 'virtual' or 'effective' bath of the particle m.

From a quantitative viewpoint if one uses to assess the function

$$\xi_0(\omega) = \cfrac{1}{-i\omega + \cfrac{\Delta_1^2}{-i\omega + \cfrac{\Delta_2^2}{-i\omega + \xi_M(\omega)}}}, \tag{91}$$

the Rahman value for Δ_1^2 of $50\times 10^{24}\ \mathrm{s}^{-2}$, and for Δ_2^2 a value related to Δ_1^2 via a Debye distribution $(\rho(\omega) = 3\omega^2/\omega_D^3$, then the frequency ω_f is overweighted in comparison with the computer simulation results. It is evident that the Mori expansion provides an elastic behaviour more intense than the Rahman simulation. One might try to improve the results by reducing the intensity of the elastic constant, i.e. by assuming that

$$\Delta_2 \ll \xi_M(\omega). \tag{92}$$

This allows us to replace the contribution $\Delta_2^2/(-\mathrm{i}\omega + \hat{\xi}_M(\omega))$ with the damping $\Delta_2^2/\hat{\xi}_M(\omega)$ independent of the frequency except via $\hat{\xi}_M(\omega)$. Equation (88) is roughly satisfied for any value of the frequency when:

$$\Delta_1 \ll \Delta_2^2/\hat{\xi}_M(\omega) \tag{93}$$

and the Rahman correlation function and spectrum are reproduced well. However this means that

$$\Delta_1 \gg (M/m)\xi_M(\omega) \tag{94}$$

and

$$\Delta_1 \ll \xi_M(\omega). \tag{95}$$

In order that both eqs. (94) and (95) are satisfied then $M \ll m$ and $\Delta_1^2 \ll \Delta_2^2$. This is inconsistent, however, with the Debye distribution, which implies

$$\Delta_1^2 = \frac{21}{4}\Delta_2^2.$$

However, in general

$$\Delta_1^2 = \langle\omega^2\rangle,$$
$$\Delta_2^2 = [\langle\omega^4\rangle - \langle\omega^2\rangle^2]/\langle\omega^2\rangle,$$

and if $\langle\omega^4\rangle \gg \langle\omega^2\rangle^2$ the Rahman results are satisfied. This means that the mean square rate of change of force in the single particle theory is much greater than the mean square force itself. This is consistent with the results obtained by using three variable Mori theory for the description of rotational motions and far infra-red spectra.

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