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The mutual interaction of molecular rotation and translation

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The dynamics of molecular rototranslation are treated with an equation of motion with a non-Markovian, stochastic force/torque. It is shown that this Mori/Kubo/Zwanzig representation is equivalent to a multidimensional Markov equation which may be identified with analytical models of the molecular motion. Langevin and Fokker–Planck equations for two such models are derived from the general equations of motion. The analytical results are compared with a computer simulation of the velocity/angular velocity mixed autocorrelation function, $C_{v\omega}(t) = \langle \mathbf{v}(0) \, . \, \boldsymbol{\omega}(t) \rangle$ for a triatomic of C_{2v} symmetry.

1. Introduction

It is the intention of this paper to demonstrate that the approach to the interpretation of spectral bandshapes dependent on molecular orientational correlation functions is incomplete without an adequate account of rotation/translation interdependence. Recent research into this topic [1–7] has tended to concentrate on the analytical aspects of the problem without reference to spectral information and computer simulation. The latter provides data which are particularly useful in revealing the behaviour of the mixed R/T autocorrelation functions. Evans [3] has recently produced a theory where the single particle R/T motions of linear diatomics are treated by a perturbation method based on modified Fokker/Planck equations. The torque correlation function contains a contribution from R/T interaction and cannot be calculated adequately by fixing the centre of mass as in the classical hydrodynamical equations of motion. Molecular angular momentum is no longer consistent with a linear Langevin equation, because orientation as well as momentum changes during a collision. Classical Brownian theory consistently overestimates the rotational drag on a body by neglecting translational motions which can partially relieve the torque. Similarly stochastic rotations reduce translational drag. This diminution is set against the expectation that R/T interaction has the nett effect of strongly enhancing the *overall* frictional drag. Wolynes and Deutch have considered the R/T interaction for multiparticle brownian motion as described by the coupled Langevin equations [2]. These authors have observed, together with Berne and Montgomery [1], that in dilute solutions of spherical

Brownian particles R/T interaction plays a fundamental role which cannot be neglected in many particle systems. R/T interaction appears both at the single and multiparticle levels because the relevant correlation functions are linked in principle by a series of macro–micro correlation theorems which we shall attempt to derive in future work.

This paper is developed as follows. In § 2 we specialize for use with molecular rototranslation (or transrotation) the stochastic Liouville equation as written by Zwanzig, Kubo and others in a form which happens to be similar to (and is therefore often referred to [8] as the generalized) Langevin equation. This non-Markovian equation is replaced in § 2 with a multidimensional Markov equation easily interpretable [9] in terms of analytical models of the molecular dynamics. Section 3 discusses two such models, the rototranslational Langevin equations and itinerant oscillation/libration [7, 10]. These may also be written as Fokker–Planck equations for the two point probability density functions. The autocorrelation matrix is derived using the equivalence of the models to approximants of the multidimensional Mori continued fraction. Section 4 compares the analytical results with far infrared power absorption. Finally, in § 5 we discuss the consequences for dielectric/far infrared spectral analysis of replacing the obsolete rotational theories with those fully descriptive of R/T interaction. We indicate possible lines of development within the methodological triangle of analytical theory, computer simulation and spectral investigation.

Section 2

According to the projection operator method [11] the Liouville equation may be replaced by a generalized master equation involving only that part of the distribution function which is of interest. Using a quantum mechanical approach the distribution function will be replaced by a density matrix. If the projection operator is just the one defining the subspace spanned by the variable $\mathbf{A}$, such a generalized equation may be used to obtain the time evolution of $\mathbf{A}$. This approach then results in the equation

$$\dot{\mathbf{A}}(t) = i\boldsymbol{\Omega}_{\mathbf{A}} \,.\, \mathbf{A}(t) - \int_0^t d\tau\, \phi_{\mathbf{A}}(t-\tau)\mathbf{A}(\tau) + \mathbf{F}_{\mathbf{A}}(t). \tag{1}$$

Here $\boldsymbol{\Omega}_{\mathbf{A}}$ is a resonance frequency operator, the matrix kernel $\phi_{\mathbf{A}}(t)$ is the effective liouvillian referred to as the memory function, and $\mathbf{F}_{\mathbf{A}}(t)$ is a generalized random force or torque propagated by projection from $\mathbf{A}(0)$ on to the relevant Hilbert space. These quantities are specified in terms of projection operators $\hat{P}$, $\hat{Q}$

$$\left.\begin{aligned} \hat{P}\mathbf{G} &= \langle G\mathbf{A}^T(0)\rangle\langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle^{-1}\,\mathbf{A}(0), \\ \hat{Q} &= \hat{1} - \hat{P}, \end{aligned}\right\} \tag{2}$$

where $\hat{P}$ projects an arbitrary vector $\mathbf{G}$ into the subspace spanned by $\mathbf{A}(0)$, and $\hat{Q}$ projects on to the orthogonal complement of this subspace. The appropriate relations are

$$\begin{aligned} i\boldsymbol{\Omega}_{\mathbf{A}} &= \langle \dot{\mathbf{A}}(0)\mathbf{A}^T(0)\rangle\langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle^{-1}, \\ \mathbf{F}_{\mathbf{A}}(t) &= \exp(i\hat{Q}\mathscr{L}t)\hat{Q}\dot{\mathbf{A}}(0), \\ \boldsymbol{\phi}_{\mathbf{A}}(t) &= \langle \mathbf{F}_{\mathbf{A}}(t)\mathbf{F}_{\mathbf{A}}{}^T(0)\rangle\langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle^{-1}. \end{aligned}$$

The simplest physical realizations of equation (1) occur, for example, in the rotational brownian motion of a space fixed spherical top, or a space-fixed disc rotating about a fixed axis through its centre perpendicular to its plane. Equation (1) then becomes

$$\frac{D\mathbf{J}}{Dt} + \int_0^t d\tau\, \phi_{\mathbf{J}}(t-\tau)\mathbf{J}(\tau) = \mathbf{F}_{\mathbf{J}}(t), \tag{3}$$

where $\mathbf{A} = \mathbf{J}$ is the angular momentum of the rotator, the operator $i\boldsymbol{\Omega}_{\mathbf{J}}$ is null, $\phi_{\mathbf{J}}(t)$ is a time-dependent friction tensor, and $\mathbf{F}_{\mathbf{J}}(t)$ is a random driving torque of finite correlation time with mean $\langle \mathbf{F}_{\mathbf{J}}(t)\rangle = 0$. In equation (3) the components of each vector are referred to principal body-axes, and D/Dt denotes rate of change relative to these axes, so that $D\hat{J}_k/Dt = J_k$. In the case of the disc (or the asymmetric top dipole librating in a plane with fixed centre of mass) there is only one component, referred to the fixed axis. For more complicated geometries *non-linear terms* appear in equation (3). The more general angular (space fixed) equation

$$\dot{\mathbf{J}}(t) - i\boldsymbol{\Omega}_{\mathbf{J}} \,.\, \mathbf{J}(t) + \int_0^t d\tau\, \phi_{\mathbf{J}}(t-\tau)\mathbf{J}(\tau) = \mathbf{F}_{\mathbf{J}}(t) \tag{4}$$

is formally valid for the asymmetric top, but then the quantities $i\boldsymbol{\Omega}_{\mathbf{J}}$, $\phi_{\mathbf{J}}$ and $\mathbf{F}_{\mathbf{J}}$ may not have any obvious physical meaning in three-dimensional space.

We shall show in this section that equation (1) may be replaced by a Markovian equation

$$\frac{d}{dt}\mathbf{V} = i\boldsymbol{\omega} \,.\, \mathbf{V} - \boldsymbol{\alpha} \,.\, \mathbf{V} - \boldsymbol{\sigma} \,.\, \mathbf{V} + \Psi(t), \tag{5}$$

where $\mathbf{V}$ can be regarded as an n-dimensional column vector of m components, which are, in turn, m-dimensional vectors. So we write

$$\mathbf{V} = \begin{bmatrix} \mathbf{A}_1 \\ \mathbf{A}_2 \\ \vdots \\ \mathbf{A}_n \end{bmatrix}, \tag{6}$$

$\boldsymbol{\omega}$ is a diagonal matrix of submatrices, defined as

$$\boldsymbol{\omega} = \begin{bmatrix} \boldsymbol{\Omega}'_1 & \mathbf{0} & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\Omega}'_2 & \mathbf{0} & \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{\Omega}'_3 & & \vdots \\ \mathbf{0} & \mathbf{0} & \mathbf{0} & & \boldsymbol{\Omega}'_n \end{bmatrix}. \tag{7}$$

The matrix $\boldsymbol{\alpha}$ is defined as

$$\boldsymbol{\alpha} = \begin{bmatrix} \mathbf{0} & \boldsymbol{\omega}_{12} & \mathbf{0} & \dots & \mathbf{0} \\ \boldsymbol{\omega}_{21} & \mathbf{0} & \boldsymbol{\omega}_{23} & \dots & \mathbf{0} \\ \mathbf{0} & \boldsymbol{\omega}_{32} & \mathbf{0} & \boldsymbol{\omega}_{34} \dots & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \boldsymbol{\omega}_{43} & \mathbf{0} & \boldsymbol{\omega}_{45} \dots \\ \vdots & \vdots & \vdots & \vdots & \vdots \end{bmatrix}. \tag{8}$$

The matrix $\boldsymbol{\sigma}$ and the vector $\boldsymbol{\Phi}$ may be written as

$$\boldsymbol{\sigma}=\begin{bmatrix}\boldsymbol{\gamma} & \mathbf{0} & \cdots\\ \mathbf{0} & \mathbf{0} & \cdots\\ \vdots & \vdots & \end{bmatrix};\quad \boldsymbol{\Psi}=\begin{bmatrix}\mathbf{F}(t)\\ \mathbf{0}\\ \vdots\end{bmatrix}. \tag{9}$$

The Laplace transform of the memory kernel $\tilde{\boldsymbol{\phi}}(p)$ may be written as

$$\frac{1}{\ddots}\cdot\frac{1}{\boldsymbol{\Delta}_{n-2}^{2}+\mathbf{1}p-i\boldsymbol{\Omega}_{n-1}}\cdot\boldsymbol{\Delta}_{n-1}^{2}=\tilde{\boldsymbol{\phi}}(p).$$

$$\frac{1}{\mathbf{1}p-i\boldsymbol{\Omega}_1+\boldsymbol{\gamma}}\,\boldsymbol{\Delta}_1^{2}+\mathbf{1}p-i\boldsymbol{\Omega}_2 \tag{10}$$

We shall derive equation (5) by the technique of induction developed recently by Ferrario and Grigolini [9] for scalar A_i.

Proof

For the case $n=1$ we have $\boldsymbol{\Omega}'_1=\boldsymbol{\Omega}$ and

$$\frac{d}{dt}\mathbf{A}_1=i\boldsymbol{\Omega}'_1\cdot\mathbf{A}_1-\boldsymbol{\gamma}\cdot\mathbf{A}_1+\mathbf{F}(t). \tag{11}$$

The fluctuation–dissipation theorem reads :

$$\begin{aligned}\langle\mathbf{F}(t)\mathbf{F}^T(s)\rangle&=\boldsymbol{\phi}_1(t)\cdot\langle\mathbf{A}_1(0)\mathbf{A}_1{}^T(0)\rangle,\\ &=2\boldsymbol{\gamma}\cdot\delta(t-s)\cdot\langle\mathbf{A}_1(0)\mathbf{A}_1{}^T(0)\rangle.\end{aligned} \tag{12}$$

The brackets $\langle\ \rangle$ define the stochastic average (or, in the quantum mechanical case, the average over the corresponding quantum mechanical canonical distribution). By following the induction method, we assume the theorem to be satisfied in the $(n-1)$ dimensional case. The n-dimension case can then be reproduced as follows :

$$\frac{d}{dt}\mathbf{A}_{n-1}=i\boldsymbol{\Omega}_{n-1}\cdot\mathbf{A}_{n-1}(t)-\int_0^t\boldsymbol{\phi}_{n-1}(t-\tau)\cdot\mathbf{A}_{n-1}(\tau)\,d\tau+\mathbf{f}_{n-1}(t)+\boldsymbol{\omega}_{n-1,n}\cdot\mathbf{A}_n, \tag{13}$$

$$\frac{d\mathbf{A}}{dt}=i\boldsymbol{\Omega}'_n\cdot\mathbf{A}_n+\boldsymbol{\omega}_{n,n-1}\cdot\mathbf{A}_{n-1}. \tag{14}$$

Laplace transforming we obtain

$$\tilde{\boldsymbol{\phi}}_n(p)=-\boldsymbol{\omega}_{n,n-1}\cdot(p\mathbf{1}-i\boldsymbol{\Omega}'_{n-1}+\tilde{\boldsymbol{\phi}}_{n-1}(p))^{-1}\cdot\boldsymbol{\omega}_{n-1,n} \tag{15}$$

and

$$\tilde{\mathbf{f}}_n(p)=\boldsymbol{\omega}_{n,n-1}\cdot(p\mathbf{1}-i\boldsymbol{\Omega}'_{n-1}+\tilde{\boldsymbol{\phi}}_{n-1}(p))^{-1}\cdot(\mathbf{A}_{n-1}(0)+\tilde{\mathbf{f}}_{n-1}(p)). \tag{16}$$

In order to obtain an exact agreement with the formulae of Mori we must assume that

$$\boldsymbol{\Omega}'_n=\boldsymbol{\Omega}, \tag{17}$$

$$\boldsymbol{\Omega}'_{n-1}=\boldsymbol{\Omega}_{n-1}. \tag{18}$$

The matrix $\boldsymbol{\alpha}$ has to be written, furthermore, as

$$\boldsymbol{\alpha}=\begin{bmatrix}\mathbf{0} & -\boldsymbol{\Delta}_1^{2} & \mathbf{0} & \mathbf{0} & \cdots\\ \mathbf{1} & \mathbf{0} & -\boldsymbol{\Delta}_2^{2} & \mathbf{0} & \cdots\\ \mathbf{0} & \mathbf{1} & \mathbf{0} & -\boldsymbol{\Delta}_3^{2} & \cdots\\ \vdots & \vdots & \vdots & \vdots & \end{bmatrix}. \tag{19}$$

We emphasize that in the course of the present demonstration we are obliged to give the matrix $\boldsymbol{\alpha}$ a form which is not the antisymmetrical one of the monodimensional case [9]. However, it is easy to show that in the multidimensional case we have $\langle\mathbf{V}(\boldsymbol{\alpha}\mathbf{V})^T\rangle=\mathbf{0}$. In fact, the structure of the $\boldsymbol{\alpha}$ matrix is such that it contains mixtures of vector components belonging to different spaces. We may identify $\mathbf{V}_i$ $(i<n)$ with an additional Mori variable and notice that the additional variables are orthogonal to the old ones.

In the same way as we may derive the fluctuation–dissipation theorem and show that for any n-dimensional case we have

$$\langle\mathbf{f}_n(t)\mathbf{f}_n{}^T(s)\rangle=\boldsymbol{\phi}_n(t-s)\langle\mathbf{A}_n(0)\mathbf{A}_n{}^T(0)\rangle. \tag{20}$$

Equation (12) shows that such a condition is satisfied in the case where $n=1$. Assuming (20) is satisfied in the $(n-1)$ dimension case, and using (16) we could write the double Laplace transform of

$$\begin{aligned}&\langle\mathbf{f}_n(t)\mathbf{f}_n{}^T(s)\rangle\quad\text{as}\quad\langle\tilde{\mathbf{f}}_n(p)\tilde{\mathbf{f}}^T(q)\rangle\\ &=\frac{1}{p+q}\{\boldsymbol{\phi}_n(p)\cdot\langle\mathbf{A}_n(0)\mathbf{A}^T(0)\rangle+\langle\mathbf{A}_n(0)\mathbf{A}_n{}^T(0)\rangle\cdot\tilde{\boldsymbol{\phi}}_n{}^T(q)\}\\ &=\frac{1}{p\mathbf{1}-i\boldsymbol{\Omega}_{n-1}+\tilde{\boldsymbol{\phi}}_{n-1}(p)}\cdot\langle(\mathbf{A}_{n-1}(0)+\mathbf{f}_{n-1}(0))\cdot(\mathbf{A}_{n-1}(0)+\mathbf{f}_{n-1}(0))^T\rangle\\ &\qquad\cdot\left(\frac{1}{q\mathbf{1}-i\boldsymbol{\Omega}_{n-1}+\boldsymbol{\phi}_{n-1}(q)}\right)^T.\end{aligned} \tag{21}$$

In order to obtain this equation we have used the property of the ' memory kernel '

$$\boldsymbol{\phi}(t-s)\cdot\langle\mathbf{A}\mathbf{A}^T\rangle=\langle\mathbf{A}\mathbf{A}^T\rangle\cdot\boldsymbol{\phi}^T(s-t). \tag{22}$$

In order that (21) be satisfied, one requires :

$$\langle\mathbf{A}_{n-1}(0)\mathbf{A}_{n-1}{}^T(0)\rangle=\boldsymbol{\Delta}_{n-1}{}^2\cdot\langle\mathbf{A}_n(0)\mathbf{A}_n{}^T(0)\rangle. \tag{23}$$

As we have pointed out already (23) corresponds to relating the variable $\mathbf{A}_n$, $\mathbf{A}_{n-1}$ and so on with the additional variable of Mori, $\mathbf{f}_i$. Using the van Kampen lemma

$$\frac{\partial p_2{}^{(\omega)}}{\partial t}=\operatorname{div}\dot{\mathbf{V}}p_2{}^{(\omega)}+\Gamma_L p_2{}^{(\omega)}, \tag{24}$$

where $p_2{}^{(\omega)}$ is the multidimensional two point probability density function, we can find the Fokker–Planck equation corresponding to (5). The parameter

Γ_L may be found by reference to Fox and Uhlenbeck [12]. So we may write

$$\frac{\partial p_2^{(\omega)}}{\partial t}(\mathbf{V}(t_2), t_2;\ \mathbf{V}(t_1), t_1)$$
$$= \sum_{i,j=1}^{n} \frac{\partial}{\partial \mathbf{A}_i(t_2)} (-i\Omega_i\delta_{ij} + \alpha_{ij}) \cdot \mathbf{A}_j(t_2) p_2(\ldots) + \frac{\partial}{\partial \mathbf{A}_1(t_2)} \Upsilon \cdot \mathbf{A}_1(t_2) p_2(\ldots)$$
$$+ \frac{\partial}{\partial \mathbf{A}_1(t_2)} \tfrac{1}{2} (\Upsilon \cdot \langle \mathbf{A}_1(0)\mathbf{A}_1^T(0)\rangle + \langle \mathbf{A}_1(0)\mathbf{A}_1^T(0)\rangle \cdot \Upsilon)$$
$$\times \frac{\partial}{\partial \mathbf{A}_1(t_2)} p_2(\ldots), \quad (25)$$

which may be associated with equation (1) through a suitable contraction process, over the variables $\mathbf{A}_1$ to $\mathbf{A}_{n-1}$. Explicit expressions for Δ_i, Ω_i and $\mathbf{V}$ are obtainable from the well-known work by Mori [13], i.e.

$$i\Omega_i = \langle \dot{\mathbf{A}}_i(0)\mathbf{A}_i^T(0)\rangle \cdot \langle \mathbf{A}_i(0)\mathbf{A}_i^T(0)\rangle^{-1} \quad (26)$$

and (nth order truncation):

$$\Upsilon = \int_0^\infty dt\, \langle \mathbf{f}_n^{(m)}(t)\mathbf{f}_n^{(m)T}(0)\rangle \langle \mathbf{f}_{n-1}^{(m)}(0)\mathbf{f}_{n-1}^{(m)}(0)^T\rangle^{-1}. \quad (27)$$

Equation (25) is directly comparable with the Fokker–Planck equation obtained by Davies and Evans [14] from the non-Markovian equation (1)

$$\frac{\partial p}{\partial t}(\mathbf{A};\ t|\mathbf{A}(0)) = -\frac{\partial}{\partial \mathbf{A}} \cdot (C_\mathbf{A} C_\mathbf{A}^{-1} \mathbf{A}_p) + \tfrac{1}{2} \frac{\partial}{\partial \mathbf{A}} \cdot \left[C_\mathbf{A} \frac{d}{dt} (m^{-1}) C_\mathbf{A}^T \frac{\partial p}{\partial \mathbf{A}} \right], \quad (28)$$

where $C_\mathbf{A}$ is the correlation matrix of $\mathbf{A}$ and m is related to the variance–covariance matrix (Appendix C). The approach by Fox [12] and Adelman [15], Davies and Evans [14] and the one by Ferrario and Grigolini may be considered as being equivalent in that both result in equation (28), as has been checked in the case of a monodimensional variable [9]. Particular forms of (28) have been discussed by Adelman [15] when the elements of $\mathbf{A}$ are uncorrelated, and for phase space variables of the form

$$\mathbf{A} = \begin{bmatrix} \mathbf{a} \\ \dot{\mathbf{a}} \end{bmatrix}.$$

Equation (5) is a very useful form for developing rototranslational models as approximants of the continued fraction (equation (10)). The inclusion of translation provides a severe test of the self-consistency of any such approximant. Ferrario and Grigolini [9] have shown that odd approximants may be chosen so as to reproduce exactly itinerant oscillator models where successive cages of molecules are brought into the dynamical 'orbit' of a central molecule. In § 2 we illustrate these modelling techniques by using (5) to build up rototranslational equations of motion formally equivalent to approximants of equation (10).

Section 3

In this section we illustrate the grand-matrix representation of the Mori equation developed in § 2 by reference to rotation/translation coupling. Note that the methods of § 2 are quite general and provide us with a very powerful theoretical formalism for use in other fields of investigation.

The first approximant of equation (10) corresponds to (5) in the form

$$\left.\begin{aligned} \dot{\mathbf{A}}_1 &= -\boldsymbol{\omega}_{12} \cdot \mathbf{A}_2 - \Upsilon \cdot \mathbf{A}_1 + \mathbf{F}(t), \\ \mathbf{A}_2 &= \mathbf{0}. \end{aligned}\right\} \quad (29)$$

Consider now the rototranslational diffusion in space of a single molecule which is a spherical top with an embedded dipole, a disc-like symmetric top, or an asymmetric top with the dipole axis constrained to rotate in a plane. Then we may write

$$\mathbf{A} = \begin{bmatrix} m\mathbf{v} \\ I\boldsymbol{\omega} \end{bmatrix},$$

where $\mathbf{v}$ is the centre of mass velocity, and $\boldsymbol{\omega}$ the angular velocity of the rotating body referred to a fixed axis through the centre of mass. m is the mass, I the relevant component of the inertial dyadic. We write

$$\mathbf{F} = \begin{bmatrix} \mathbf{F} \\ \mathbf{T} \end{bmatrix},$$

where $\mathbf{F}$ and $\mathbf{T}$ are stochastic force and torque. In general we set

$$\Upsilon = \begin{bmatrix} \Upsilon_t & \Upsilon_{tr} \\ \Upsilon_{rt} & \Upsilon_r \end{bmatrix}, \quad (30)$$

where Υ_t and Υ_r are diagonal frictional drag (units of frequency) tensors which reduce to scalars for the sphere and disc. The off-diagonal elements of Υ are rototranslational and may be interpreted for single particle motion in terms of the ability [3, 4] of stochastic translational motion to relieve the torque and stochastic rotational motions to relieve the force on the moving molecule. Equation (30) could be written as (Appendix B)

$$\Upsilon = \begin{bmatrix} \Upsilon_t & -\Upsilon_{tr} \\ -\Upsilon_{rt} & \Upsilon_r \end{bmatrix}, \quad (31)$$

if Υ_{tr} and Υ_{rt} are to be regarded as positive frequency terms. However, we shall retain in this paper the notation of (30). The numerically negative off diagonal elements of Υ seem to be indicative of Evans's description [3] that the classical Brownian theory overestimates rotational drag or translational drag when considered in isolation. (See Appendix B.)

The general case of a three-dimensional asymmetric top motion is complicated by the fact that the angular velocity components cannot be related to the orientation vector in a linear fashion. (The relation is simpler for the sphere and needle.) Using Eulerian angles to define the orientation time dependence

it is preferable to express the dynamical equations in the rotating frame of reference fixed in the body under consideration [15 (b)]. A precessional contribution has then to be added to the dynamical equations. In the case where the vector variable **A** contains an angular momentum component such as $\mathbf{I}\,.\,\boldsymbol{\omega}$, it would be convenient to perform such a transformation by replacing (5) with one modified by the inclusion of a precessional term which is non-linear in **A**. Such a modification does not avoid, however, the main difficulties of the problem under discussion. The memory kernel of the Mori theory is intractable in general ; and even in the Markov limit, we obtain :

$$\left.\begin{aligned}\dot{\omega}_i &= \frac{(I_j - I_k)}{I_i}\,\omega_j\omega_k - \sum_{l=1}^{3}\left(\gamma_{il}^{(\mathrm{r})}\,\omega_l + \gamma_{il}^{(\mathrm{rt})}\,v_l\right) + \tilde{\Gamma}_i(t),\\ \dot{v}_i &= -\sum_{l=1}^{3}\left(\gamma_{il}^{(\mathrm{t})}\,v_l + \gamma_{il}^{(\mathrm{tr})}\,\omega_l\right) + \tilde{F}_i(t),\end{aligned}\right\} \tag{32}$$

where i, j, k are cyclic permutations of 1, 2 and 3. The presence of the non-linear terms in (32) prevents the use of Laplace methods of solution. Importantly, however, the methods developed by Ferrario and Grigolini allow us to write down the corresponding Fokker–Planck rototranslational equation (see Appendix A) which may be solved numerically for the probability density function p_2 and the relevant spectra extracted by numerical integration and Fourier transformation. For p_2 we may write

$$\begin{aligned}&\frac{\partial p_2}{\partial t}(\mathbf{v}, \boldsymbol{\omega}, t\,|\,\mathbf{v}_0, \boldsymbol{\omega}_0, t_0)\\ &= \sum_{l=1}^{3}\left\{-\left[\frac{\partial}{\partial\omega_i}\left(\frac{I_j - I_k}{I_i}\right)\omega_j\omega_k p_2\right]\right.\\ &\quad + \sum_{l=1}^{3}\left[\frac{\partial}{\partial\omega_i}\left(\gamma_{il}^{(\mathrm{r})}\,\omega_l + \gamma_{il}^{(\mathrm{rt})}\,v_l\right) + \frac{\partial}{\partial v_i}\left(\gamma_{il}^{(\mathrm{t})}\,v_l + \gamma_{il}^{(\mathrm{tr})}\,\omega_l\right)\right]p_2\\ &\quad + \sum_{l=1}^{3}\frac{\partial}{\partial\omega_i}\left[\gamma_{il}^{(\mathrm{r})}\frac{kT}{I_i}\frac{\partial}{\partial\omega_l} + \tfrac{1}{2}\left(\gamma_{il}^{(\mathrm{tr})}\frac{kT}{I_i} + \gamma_{il}^{(\mathrm{rt})}\frac{kT}{m}\right)\frac{\partial}{\partial v_l}\right]p_2\\ &\quad \left. + \sum_{l=1}^{3}\frac{\partial}{\partial v_i}\left[\gamma_{il}^{(\mathrm{t})}\frac{kT}{m}\frac{\partial}{\partial v_l} + \tfrac{1}{2}\left(\gamma_{il}^{(\mathrm{rt})}\frac{kT}{m} + \gamma_{il}^{(\mathrm{tr})}\frac{kT}{I_i}\right)\frac{\partial}{\partial\omega_l}\right]p_2\right\},\end{aligned} \tag{33}$$

i, j, k again permute 1, 2, 3 cyclically.

Equation (29) may be written, using (30) and the above definition of **A** and **F** as

$$\left.\begin{aligned}m\dot{\mathbf{v}} &= -m\gamma_{\mathrm{t}}\mathbf{v} - \gamma_{\mathrm{tr}}I\boldsymbol{\omega} + \mathbf{F},\\ I\dot{\boldsymbol{\omega}} &= -I\gamma_{\mathrm{r}}\boldsymbol{\omega} - \gamma_{\mathrm{rt}}m\mathbf{v} + \mathbf{T}.\end{aligned}\right\} \tag{34}$$

These are the single-particle rototranslational Langevin equations for the sphere or disc. They are applicable in this form to asymmetric top rototranslation under the following conditions :

(1) the centre of mass velocity is

$$\mathbf{v} = \begin{bmatrix} v_x\\ v_y\\ v_z\end{bmatrix}.$$

(2) the angular velocity is

$$\boldsymbol{\omega} = \begin{bmatrix} 0\\ 0\\ \omega_z\end{bmatrix} \text{ (planar) ;}$$

(3) γ_{t} is regarded as a scalar, the mean translational friction coefficient. Using three coefficients will complicate the comparison with experimental data ;

(4) in general $\boldsymbol{\gamma}_{\mathrm{r}}$ is a 3×3 matrix (diagonalized) :

$$\boldsymbol{\gamma}_{\mathrm{r}} = \begin{bmatrix} \gamma_{\mathrm{r}}^{(xx)} & 0 & 0\\ 0 & \gamma_{\mathrm{r}}^{(yy)} & 0\\ 0 & 0 & \gamma_{\mathrm{r}}^{(zz)}\end{bmatrix};$$

(5) $\boldsymbol{\gamma}_{\mathrm{rt}}$ and $\boldsymbol{\gamma}_{\mathrm{tr}}$ are diagonal matrices defined similarly. The solution of (34) in terms of autocorrelation functions may be written down from the continued fraction (10) in terms of the transpose matrix

$$\mathbf{C}(t) = \begin{bmatrix} \langle\mathbf{v}(t)\mathbf{v}^T(0)\rangle\langle\mathbf{v}(0)\mathbf{v}^T(0)\rangle^{-1} & \langle\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle\langle\boldsymbol{\omega}(0)\boldsymbol{\omega}^T(0)\rangle^{-1}\\ \langle\boldsymbol{\omega}(t)\mathbf{v}^T(0)\rangle\langle\mathbf{v}(0)\mathbf{v}^T(0)\rangle^{-1} & \langle\boldsymbol{\omega}(t)\boldsymbol{\omega}^T(0)\rangle\langle\boldsymbol{\omega}(0)\boldsymbol{\omega}^T(0)\rangle^{-1}\end{bmatrix}. \tag{35}$$

Denoting $\boldsymbol{\Delta}_{n-1}{}^2(0) = \boldsymbol{\phi}_1(0)$, $\boldsymbol{\Delta}_{n-2}{}^2(0) = \boldsymbol{\phi}_2(0)$, etc., we have :

$$\begin{aligned}\tilde{\mathbf{C}}(s) &= [s + \tilde{\mathbf{C}}_1(s)\,.\,\boldsymbol{\phi}_1(0)]^{-1}\\ &= [s + [s + \tilde{\mathbf{C}}_2(s)\,.\,\boldsymbol{\phi}_2(0)]^{-1}\,\boldsymbol{\phi}_1(0)]\\ &= \ldots,\end{aligned} \tag{36}$$

where $\boldsymbol{\phi}_1(s) = \tilde{\mathbf{C}}_1(s)\,.\,\boldsymbol{\phi}_1(0)$ and $\boldsymbol{\phi}_2(s) = \tilde{\mathbf{C}}_2(s)\,.\,\boldsymbol{\phi}_2(0)$ etc. are the Laplace transforms of the first and second memory matrices, and the $\boldsymbol{\phi}_j(0)$ are defined by

$$\left.\begin{aligned}&\boldsymbol{\phi}_j(0) = \langle\mathbf{f}_j\mathbf{f}_j{}^T\rangle\langle\mathbf{f}_{j-1}\mathbf{f}_{j-1}{}^T\rangle^{-1}\\ &\text{with}\quad \mathbf{f}_0 = \begin{bmatrix}\mathbf{v}(0)\\ \boldsymbol{\omega}(0)\end{bmatrix};\quad \mathbf{f}_1 = \begin{bmatrix}\dot{\mathbf{v}}(0)\\ \dot{\boldsymbol{\omega}}(0)\end{bmatrix}\\ &\text{and}\quad \mathbf{f}_2 = \begin{bmatrix}\ddot{\mathbf{v}}(0) + \dfrac{\langle\dot{V}^2(0)\rangle}{\langle V^2(0)\rangle}\,\mathbf{v}(0)\\ \ddot{\boldsymbol{\omega}}(0) + \dfrac{\langle\dot{\omega}^2(0)\rangle}{\langle\omega^2(0)\rangle}\,\boldsymbol{\omega}(0)\end{bmatrix}.\end{aligned}\right\} \tag{37}$$

We find that

$$\boldsymbol{\phi}_j(0) = \begin{bmatrix}\phi_{\mathrm{t}_j} & 0\\ 0 & \phi_{\mathrm{r}_j}\end{bmatrix},$$

where

$$\phi_{t_1}=\frac{\langle\dot{v}^2(0)\rangle}{\langle v^2(0)\rangle}; \qquad \phi_{r_1}=\frac{\langle\dot{\omega}^2(0)\rangle}{\langle\omega^2(0)\rangle}$$

$$\phi_{t_2}=\frac{\langle\ddot{v}^2(0)\rangle}{\langle\dot{v}^2(0)\rangle}-\frac{\langle\dot{v}^2(0)\rangle}{\langle v^2(0)\rangle}; \quad \phi_{r_2}=\frac{\langle\ddot{\omega}^2(0)\rangle}{\langle\dot{\omega}^2(0)\rangle}-\frac{\langle\dot{\omega}^2(0)\rangle}{\langle\omega^2(0)\rangle}.$$

As we shall see (*vide infra*) these latter terms are identical with the corresponding ones in the (decoupled) planar itinerant oscillator or librator models. The solution for Langevin type rototranslation may be found if we define

$$\tilde{\mathbf{C}}_1(s)\,.\,\boldsymbol{\phi}_1(0)=\begin{bmatrix}\boldsymbol{\lambda}_t & \boldsymbol{\lambda}_{tr}\\ \boldsymbol{\lambda}_{rt} & \boldsymbol{\lambda}_r\end{bmatrix}, \tag{38}$$

where the λs have frequency dimensions. It follows that

$$\tilde{\mathbf{C}}(s)=\begin{bmatrix}s\mathbf{1}+\boldsymbol{\lambda}_t & \boldsymbol{\lambda}_{tr}\\ \boldsymbol{\lambda}_{rt} & s\mathbf{1}+\boldsymbol{\lambda}_t\end{bmatrix}. \tag{39}$$

3.1. *The spherical top and disc*

In this case the components of $\mathbf{v}$ and $\boldsymbol{\omega}$ are mutually statistically uncorrelated. It follows that

$$\langle v(t)v(0)\rangle=\begin{cases}\langle v^2(0)\rangle\exp(-bt)\left[\cos(c-b^2)^{1/2}t+\dfrac{\lambda_r-b}{(c-b^2)^{1/2}}\sin(c-b^2)^{1/2}t\right], & c>b^2\\ \langle v^2(0)\rangle\exp(-bt)\left[\cosh(b^2-c)^{1/2}t+\dfrac{\lambda_r-b}{(b^2-c)^{1/2}}\sinh(b^2-c)^{1/2}t\right], & c<b^2;\end{cases} \tag{40}$$

$$\langle\omega(t)v(0)\rangle=\begin{cases}-\dfrac{\langle\omega^2(0)\rangle\lambda_{tr}}{(c-b^2)^{1/2}}\exp(-bt)\sin(c-b^2)^{1/2}t, & c>b^2\\ -\dfrac{\langle\omega^2(0)\rangle\lambda_{rt}}{(b^2-c)^{1/2}}\exp(-bt)\sinh(b^2-c)^{1/2}t, & b^2<c;\end{cases}$$

with similar expressions for $\langle\omega(t)\omega(0)\rangle$ and $\langle\omega(t)v(0)\rangle$. Since $\langle v(t)\omega(0)\rangle=\langle\omega(t)v(0)\rangle$ it follows that

$$\lambda_{tr}\langle\omega^2(0)\rangle=\lambda_{rt}\langle v^2(0)\rangle, \tag{41}$$

In equation (40), $b=2(\lambda_t+\lambda_r)$; $c=\lambda_t\lambda_r-\lambda_{tr}\lambda_{rt}$.

It can be seen that the angular velocity autocorrelation function $\langle\boldsymbol{\omega}(t)\,.\,\boldsymbol{\omega}(0)\rangle$ is dependent on λ_t, λ_r, λ_{tr} and λ_{rt}, as is the velocity autocorrelation function: $\langle\mathbf{v}(t)\,.\,\mathbf{v}(0)\rangle=3\langle v_i(t)v_i(0)\rangle$, $i=x$, y or z.

When $\lambda_{tr}=\lambda_{rt}=0$ the dependence reduces to one parameter (classical Brownian motion) and the mixed autocorrelation functions vanish at all times.

When $\lambda_{tr}\neq 0$, the mixed autocorrelation functions vanish, as they should only at $t=0$, and as $t\to\infty$.

We simulate directly the mixed angular momentum/linear momentum autocorrelation function for a C_{2v} triatomic in § 4. The existence of this function implies the existence of λ_{tr} and λ_{rt} of the R/T Langevin equation and that the classical theory of purely rotational Brownian motion is incomplete.

3.2. *The asymmetric top with dipole librating in a plane*

In this case the unnormalized off-diagonal mixed terms are given by

$$\langle\mathbf{v}(t)\boldsymbol{\omega}^T(0)\rangle=\begin{bmatrix}0 & 0 & \langle v_x(t)\omega_z(0)\rangle\\ 0 & 0 & \langle v_y(t)\omega_z(0)\rangle\\ 0 & 0 & \langle v_z(t)\omega_z(0)\rangle\end{bmatrix},$$

$$\langle\boldsymbol{\omega}(t)\mathbf{v}^T(0)\rangle=\begin{bmatrix}0 & 0 & 0\\ 0 & 0 & 0\\ \langle\omega_z(t)v_x(0)\rangle & \langle\omega_z(t)v_y(0)\rangle & \langle\omega_z(t)v_z(0)\rangle\end{bmatrix}$$

The R/T interaction will manifest itself through the mixed autocorrelations $\langle v_z(t)\omega_z(0)\rangle$ and $\langle\omega_z(t)v_z(0)\rangle$.

By comparison of matrix elements

$$\begin{aligned}&\mathscr{L}[\langle v_z(t)\omega_z(0)\rangle\langle\omega_z(0)\omega_z(0)\rangle^{-1}]=-\gamma_{rt}^{(zz)}/[(s+\gamma_r^{(zz)})(s+\gamma_t)-\gamma_{rt}^{(zz)}\gamma_{tr}^{(zz)}],\\ &\mathscr{L}[\langle v_x(t)v_x(0)\rangle\langle v_x(0)v_x(0)\rangle^{-1}]=1/(s+\gamma_t),\\ &\mathscr{L}[\langle v_y(t)v_y(0)\rangle\langle v_y(0)v_y(0)\rangle^{-1}]=1/(s+\gamma_t),\\ &\mathscr{L}[\langle v_z(t)v_z(0)\rangle\langle v_z(0)v_z(0)\rangle^{-1}]=(s+\gamma_t)/[(s+\gamma_t)(s+\gamma_r^{(zz)})-\gamma_{rt}^{(zz)}\gamma_{tr}^{(zz)}],\\ &\mathscr{L}[\langle\omega_z(t)\omega_z(0)\rangle\langle\omega_z(0)\omega_z(0)\rangle^{-1}]=(s+\gamma_r^{(zz)})/[(s+\gamma_r^{(zz)})(s+\gamma_t)-\gamma_{rt}^{(zz)}\gamma_{tr}^{(zz)}].\end{aligned} \tag{42}$$

If the translation is not spatial, so that

$$\mathbf{v}=\begin{bmatrix}v_x\\ v_y\\ 0\end{bmatrix}$$

there will be no mutual effect of rotation and translation since $\boldsymbol{\omega}$ is always perpendicular to $\mathbf{v}$. Unless $\gamma_{rt}^{(zz)}$ is zero, the angular velocity autocorrelation function is no longer exponential. We note that a propeller is a symmetric top constrained to a plane rotationally, but not translationally. In the case of the propeller there is from common experience a strong R/T interaction.

3.3. *The rototranslational itinerant oscillator/librator*

The itinerant oscillator and itinerant librator models of molecular dynamics were developed following the discovery of significant new spectral features respectively using neutron scattering [16] and far infrared spectroscopy [17]. They describe the motion of an encaged molecule with the proviso that the cage is undergoing Brownian motion. Grigolini [9] has shown how successive odd approximants of the Mori continued fraction describe the addition of more cages, the outermost one of which undergoes Brownian motion. Restricting ourselves to molecule and one outer cage, equation (5) becomes

$$\left.\begin{aligned}\dot{\mathbf{A}}_1 &= -\boldsymbol{\omega}_{12} \,.\, \dot{\mathbf{A}}_2 - \boldsymbol{\gamma} \,.\, \mathbf{A}_1 + \mathbf{F}(t),\\ \dot{\mathbf{A}}_2 &= -\boldsymbol{\omega}_{21} \,.\, \mathbf{A}_1 - \boldsymbol{\omega}_{23} \,.\, \mathbf{A}_3,\\ \dot{\mathbf{A}}_3 &= -\boldsymbol{\omega}_{32} \,.\, \mathbf{A}_2 - \boldsymbol{\omega}_{34} \,.\, \mathbf{A}_4,\\ \mathbf{A}_4 &= \mathbf{0}.\end{aligned}\right\} \tag{43}$$

We now write

$$\mathbf{A}_1 = \begin{bmatrix} (\Delta_2^{(t)}/\Delta_1^{(t)})\dot{x} \\ (\Delta_2^{(r)}/\Delta_1^{(r)})\dot{\psi} \end{bmatrix}; \quad \mathbf{A}_2 = \begin{bmatrix} \Delta_2^{(t)}(X-x) \\ \Delta_2^{(r)}(\theta-\psi) \end{bmatrix}; \quad \mathbf{A}_3 = \begin{bmatrix} \dot{X} \\ \dot{\theta} \end{bmatrix}.$$

Here x is a component of the centre of mass velocity of the cage, X of the molecule, and (θ, ψ) are angles defined elsewhere [10], which describe the rotational itinerant oscillator. Substituting in (43) we find a component set of equations for itinerant libration and oscillation

$$\left.\begin{aligned}(\Delta_2^{(t)}/\Delta_1^{(t)})\ddot{x} &= \Delta_1^{(t)}\,\Delta_2^{(t)}(X-x) - (\Delta_2^{(t)}/\Delta_1^{(t)})\gamma^{(t)}\dot{x} - \gamma^{(tr)} \\ &\quad \times (\Delta_2^{(r)}/\Delta_1^{(r)})\dot{\psi} + F_x,\\ (\Delta_2^{(r)}/\Delta_1^{(r)})\ddot{\psi} &= \Delta_1^{(r)}\,\Delta_2^{(r)}(\theta-\psi) - (\Delta_2^{(t)}/\Delta_1^{(t)})\gamma^{(rt)}\dot{x} - \gamma^{(r)} \\ &\quad \times (\Delta_2^{(r)}/\Delta_1^{(r)})\dot{\psi} + T,\\ \ddot{X} &= -\Delta_2^{(t)}\,\Delta_2^{(t)}(X-x),\\ \ddot{\theta} &= -\Delta_2^{(r)}\,\Delta_2^{(r)}(\theta-\psi).\end{aligned}\right\} \tag{44}$$

These equations decouple to those for itinerant libration and oscillation in two dimensions of the components X_i of $\mathbf{X}$ and x_i of $\mathbf{x}$. The equation (44) may be solved for the autocorrelation matrix by using their equivalence to the third approximant of (10). It follows (for z components), that if we define the third memory matrix by

$$\tilde{\mathbf{C}}_3(s) \,.\, \boldsymbol{\phi}_3(0) = \begin{bmatrix} \lambda_t & \lambda_{tr} \\ \lambda_{rt} & \lambda_r \end{bmatrix}, \tag{45}$$

we find

$$\tilde{\mathbf{C}}(s) = \frac{1}{D_2(s)} \begin{bmatrix} s + \left[s + (s+\lambda_r)\dfrac{\phi_{t_2}}{D(s)}\right]\dfrac{\phi_{r_1}}{D_1(s)}; & -\dfrac{\lambda_{tr}\phi_{r_2}\phi_{r_1}}{D(s)D_1(s)} \\ -\dfrac{\lambda_{rt}\phi_{t_2}\phi_{t_1}}{D(s)D_1(s)}; & s + \left[s + (s+\lambda_t)\dfrac{\phi_{r_2}}{D(s)}\right]\dfrac{\phi_{t_1}}{D_1(s)} \end{bmatrix}, \tag{46}$$

where

$$D_1(s) = \left[s + (s+\lambda_t)\frac{\phi_{r_2}}{D(s)}\right]\left[s + (s+\lambda_r)\frac{\phi_{t_2}}{D(s)}\right] - \frac{\lambda_{tr}\lambda_{rt}\phi_{t_2}\phi_{r_2}}{D^2(s)}$$

and

$$D_2(s) = \left[s + \left[s + (s+\lambda_t)\frac{\phi_{r_2}}{D(s)}\right]\frac{\phi_{t_1}}{D_1(s)}\right]\left[s + \left[s + (s+\lambda_r)\frac{\phi_{t_2}}{D(s)}\right]\frac{\phi_{r_1}}{D_1(s)}\right] - \frac{\lambda_{tr}\lambda_{rt}\phi_{t_2}\phi_{t_1}\phi_{r_2}\phi_{r_1}}{D^2(s)D_1^2(s)},$$

$$D(s) = (s+\lambda_t)(s+\lambda_r) - \lambda_{tr}\lambda_{rt}.$$

Equation (41) is now replaced by

$$\lambda_{tr}\phi_{r_2}\phi_{r_1} = \lambda_{rt}\phi_{t_2}\phi_{t_1}. \tag{47}$$

All autocorrelation functions involve the seven independent phenomenological parameters ϕ_{t_1}, ϕ_{t_2}, ϕ_{r_1}, ϕ_{r_2}, λ_t, λ_r, and $\lambda_{tr}\lambda_{rt}$. When $\lambda_{tr} = 0$ then the determinants $D(s)$, $D_1(s)$ and $D_2(s)$ reduce to simple factors, the velocity and angular velocity autocorrelation functions become dependent on only three parameters (in each case) and the mixed autocorrelation functions vanish.

Successive odd approximants of the continued matrix fraction in this context correspond to the addition of further cages in the model of itinerant oscillation/libration.

3.4. *Far infrared power absorption* ($\alpha(\omega)$)

In the absence of internal field effects this is related to the rotational velocity autocorrelation function $\langle \dot{\mathbf{u}}(t) \,.\, \dot{\mathbf{u}}(0)\rangle$ which under certain circumstances [18] is similar to $\langle \boldsymbol{\omega}(t) \,.\, \boldsymbol{\omega}(0)\rangle$ in time dependence. Approximately, therefore

$$\alpha(\omega) \propto \int_0^\infty \frac{\langle \boldsymbol{\omega}(t) \,.\, \boldsymbol{\omega}(0)\rangle}{\langle \boldsymbol{\omega}(0) \,.\, \boldsymbol{\omega}(0)\rangle} \cos \omega t \, dt \tag{48}$$

$$= \frac{\omega(\omega^2 + \gamma_r^2 + \gamma_{tr}\gamma_{rt})}{[(\gamma_r\gamma_t - \gamma_{rt}\gamma_{tr} - \omega^2)^2 + (\gamma_t + \gamma_r)^2\,\omega^2]} \tag{49}$$

for the sphere and disc rototranslational Langevin equations. At low frequences one extracts the Debye time as

$$\tau_D \doteq \frac{(\gamma_t + \gamma_r)^2 - 2(\gamma_r\gamma_t - \gamma_{rt}\gamma_{tr})}{(\gamma_r\gamma_t - \gamma_{rt}\gamma_{tr})}, \tag{50}$$

which therefore *diverges* when $\gamma_r\gamma_t = \gamma_{rt}\gamma_{tr}$ (i.e. for strong coupling). The $\alpha(\omega)$ from (46) may be extracted by replacing s by $-i\omega$ and separating real and

imaginary parts. We end this section by writing down the Fokker–Planck equation for the itinerant oscillator/librator, viz :

$$\frac{\partial}{\partial t} P_2(\dot{X}, \dot{x}, (X-x), \dot{\theta}, \dot{\psi}, (\theta-\psi), t, \dot{X}_0, \dot{x}_0, (X_0-x_0), \dot{\theta}_0, \dot{\psi}_0, (\theta_0-\psi_0), t_0)$$
$$= \left\{ -(\dot{\theta}-\dot{\psi}) \frac{\partial}{\partial(\theta-\psi)} - (\dot{X}-\dot{x}) \frac{\partial}{\partial(X-x)} \right.$$
$$+ \left(\Delta_1^{(r)2} \frac{\partial}{\partial \dot{\theta}} - \Delta_2^{(r)2} \frac{\partial}{\partial \dot{\psi}} \right) (\phi-\psi)$$
$$\left. + \left(\Delta_1^{(t)2} \frac{\partial}{\partial \dot{X}} - \Delta_2^{(t)2} \frac{\partial}{\partial \dot{x}} \right) (X-x) \right\} P_2 + \gamma_r \left(\frac{\partial}{\partial \dot{\psi}} \dot{\psi} + \frac{kT}{I_2} \frac{\partial^2}{\partial \dot{\psi}^2} \right) P_2$$
$$+ \gamma_t \left(\frac{\partial}{\partial \dot{x}} \dot{x} + \frac{kT}{m_2} \frac{\partial^2}{\partial \dot{x}^2} \right) P_2 + \gamma_{rt} \left(\frac{\partial}{\partial \dot{x}} \dot{\psi} + \frac{kT}{m_2} \frac{\partial^2}{\partial \dot{x} \partial \dot{\psi}} \right) P_2$$
$$+ \gamma_{tr} \left(\frac{\partial}{\partial \dot{\psi}} \dot{x} + \frac{kT}{I_2} \frac{\partial^2}{\partial \dot{x} \partial \dot{\psi}} \right) P_2. \qquad (51)$$

Here m_2 and I_2 are the mass and moment of inertia respectively of the annulus, and (51) again may be solved numerically for the two point probability density functions.

Section 4

We have attempted to simulate, using the technique of molecular dynamics, the mixed momentum/angular momentum correlation function for a triatomic molecule of C_{2v} symmetry. There are indications that this correlation function is oscillatory in nature, but much larger runs are needed before satisfactory statistics can be achieved (see figure (1) for typical autocorrelation functions of this 3×3 atom–atom Lennard–Jones potential).

In figure 2 we approximate the angular velocity autocorrelation function by the rotational velocity autocorrelation function obtained by Fourier transforming the far infrared power absorption spectrum for the pseudo-spherical asymmetric top (C_{2v}) 2,2-dichloropropane. The three variable Langevin fit of λ_r, λ_t and $\lambda_{rt}\lambda_{tr}$ is shown on this figure. This is typical of the way zero–THz data have to be treated in the light of the theories of rototranslational interaction now available. The significance of rototranslation is discussed further in § 5 with regard especially to broad-band spectral analysis.

Section 5

The effect of R/T interaction in terms of the Langevin concept of molecular motion may be rationalized as follows. When more than one particle is involved Wolynes and Deutch [2] have pointed out that the origin of the coupled drag coefficients can be understood hydrodynamically in that the translational or rotational motion of one brownian particle causes a flow in the surrounding solvent. The moving solvents then exerts forces and torques on the other solute molecules. When the brownian particles are far apart they can be thought of as point centres of drag force and drag torque acting on the fluid. When

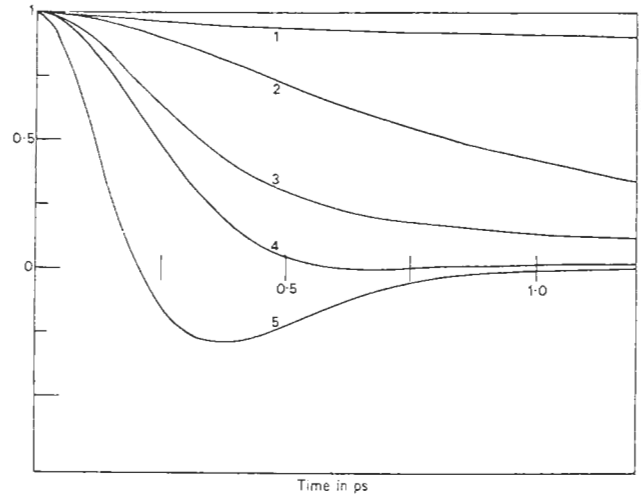

Figure 1. Autocorrelation functions calculated by molecular dynamics simulation of a C_{2v} triatomic (normalized at $t=0$). (1) Centre of mass vector ; (2) $\mathbf{e}_B$, the B inertia unit vector (i.e. orientation) ; (3) angular momentum ($\mathbf{J}$) ; (4) linear momentum ; (5) torque.

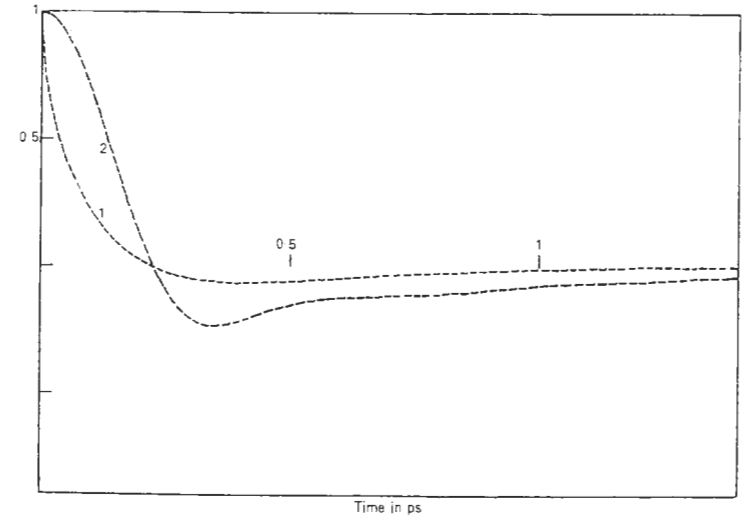

Figure 2. (1) Best fit to $\langle \dot{\mu}(t) \cdot \dot{\mu}(0) \rangle$ of 2,2-dichloropropane (liquid) [2] using λ_t, λ_r and $\lambda_{tr}\lambda_{rt}$ as variables.

the brownian particles are not interacting (as in our single particle Langevin equations of § 3) it is obvious that the flow set up in the solvent at $t=0$ by, say, a point torque, can result in a translational motion of the same molecule which would be observable *as translation* of the molecule at a time t later. A simple example is the propeller action. It is evident that for certain molecular symmetries the off-diagonal elements of γ do not vanish at finite t, i.e. there must be a mutual interaction of translation and rotation. It is, in fact, not proven in the literature that the off-diagonal elements vanish even for the highest symmetries such as that of the loaded (rough) sphere or dipolar diatomic. Arguments based on time-reversal symmetries are not enough because the probability density functions governing the mixed autocorrelation functions of interest are *conditional*. Some molecular dynamics algorithms for the solution of the equations of motion of, for example, L–J diatomics are apparently structured so that mixed autocorrelation functions are difficult to calculate. (There is an overall conservation of linear momentum, for example, so that the multiparticle and single particle velocity autocorrelation functions always decay identically. Also the imposition of boundary conditions may result in an artificial, extra, symmetry allied to the fact that there is no net flow in and out of the box). Certainly the simulated mixed autocorrelation functions of § 4 are far more difficult to stabilize than the autocorrelation functions of either component. Longer runs (exceeding the maximum available UMRCC machine time) would be helpful here. If (as suggested by Evans [3]), the torque autocorrelation function of a diatomic molecule is affected by R/T interaction, then this *analytical* conclusion should be mirrored in the results of the relevant simulation, that of L–J diatomics.

The results of § 4, where γ_t, γ_r and $\gamma_{rt}\gamma_{tr}$ are used to fit molecular dynamics and spectral data seem to indicate that the third factor is finite. The dynamics of propeller-like molecules will of course be dominated by R/T coupling. Further spectral investigation of these molecules will be helpful here. Evans [4] has shown that for certain symmetries (including C_{2v}) the function remains finite at $t \geqslant 0$. This is one of the off-diagonal elements of the first memory matrix of the vector $\begin{bmatrix} m\mathbf{v} \\ I\boldsymbol{\omega} \end{bmatrix}$ for the sphere and disc. There is therefore a mounting body of evidence to show that the idea of rotational brownian motion is misleading when dealing with spectral data such as those in the zero-THz frequency range or from light scattering. It is always possible to extract a Debye relaxation time from the loss peak but (§ 3) this is defined in terms of more parameters, rotational, translational and R/T in nature. Data from three independent sources are needed to unravel the dynamics even when memory effects are neglected. Alternatively if only one technique is available, one may use *carefully structured* non-linear fitting algorithms and choose the experimental conditions to best effect. For example, in the rotator phase of 2,2 dichloropropane λ_t is much larger than λ_r because centre of mass translation in the plastic crystal is much slower than in the liquid. Consequently a good idea of the value of λ_t may be obtained for use in analysing the liquid data.

A further complication which arises when comparing spectral data with single particle autocorrelation functions is the need for a bridging macro–micro correlation theorem. Wolynes and Deutch have initiated the study of this correlation within the context of the multi-particle diffusion equation where the

Liouville operator is split into R, T, and R/T components [2]. In the absence of memory effects they conclude that the multi and single particle correlation functions decay identically, as discussed by Madden and Kivelson [20] for pure rotational diffusion.

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Appendix A

In this Appendix we consider the derivation of the Fokker–Planck equation pertinent to

$$\frac{d\mathbf{V}}{dt} = -\mathbf{S}\mathbf{V} + \mathbf{F}, \tag{A 1}$$

where $\mathbf{S}$ is not a diagonal matrix and is related to $\mathbf{F}$ by the fluctuation dissipation theorem

$$\langle \mathbf{F}(t)\mathbf{F}^{+}(s)\rangle = 2[\mathbf{S}\mathbf{E}^{-1} + \mathbf{E}^{-1}\mathbf{S}^{+}]\delta(t-s), \tag{A 2}$$

E, the equilibrium matrix appearing in (A 2), is defined as

$$E = \langle \mathbf{V}\mathbf{V}^{+}\rangle_{eq}^{-1}. \tag{A 3}$$

The Fokker–Planck equation to be related to (A 1) is

$$\frac{\partial P_2}{\partial t} = \frac{\partial}{\partial \mathbf{V}}\mathbf{S}\mathbf{V}P_2 + \tfrac{1}{2}\frac{\partial}{\partial \mathbf{V}}(\mathbf{S}\mathbf{E}^{-1} + \mathbf{E}^{-1}\mathbf{S}^{+})\frac{\partial}{\partial \mathbf{V}}P_2 \tag{A 4}$$

In the case of R/T coupling we have

$$\left.\begin{aligned} \frac{d}{dt}\dot{\psi} &= -\gamma_r\dot{\psi} - \gamma_{rt}\dot{X} + \tilde{\Gamma}(t), \\ \frac{d}{dt}\dot{X} &= -\gamma_t\dot{X} - \gamma_{tr}\dot{\psi} + \tilde{f}(t), \end{aligned}\right\} \tag{A 5}$$

The matrix $\mathbf{E}$ is now given by

$$\mathbf{E} = \begin{bmatrix} \langle \dot{X}\dot{X}\rangle^{-1} & 0 \\ 0 & \langle \dot{\psi}\dot{\psi}\rangle^{-1} \end{bmatrix}, \tag{A 6}$$

and :

$$\tfrac{1}{2}(\mathbf{S}\mathbf{E}^{-1} + \mathbf{E}^{-1}\mathbf{S}^{+}) = \begin{bmatrix} \gamma_t\langle \dot{X}\dot{X}\rangle & \tfrac{1}{2}(\gamma_{tr}\langle \dot{\psi}\dot{\psi}\rangle + \gamma_{rt}\langle \dot{X}\dot{X}\rangle) \\ \tfrac{1}{2}(\gamma_{tr}\langle \dot{\psi}\dot{\psi}\rangle + \gamma_{rt}\langle \dot{X}\dot{X}\rangle) & \gamma_r\langle \dot{\psi}\dot{\psi}\rangle \end{bmatrix}. \tag{A 7}$$

Equation (A 4) therefore expands explicitly :

$$\begin{aligned} \frac{\partial}{\partial t}P_2 = \Bigg\{ &\left(\frac{\partial}{\partial \dot{X}}\gamma_t\dot{X} + \frac{\partial}{\partial \dot{X}}\gamma_{tr}\dot{\psi} + \frac{\partial}{\partial \dot{\psi}}\gamma_{rt}\dot{X} + \frac{\partial}{\partial \dot{\psi}}\gamma_r\dot{\psi}\right) \\ &+ \left(\frac{\partial}{\partial \dot{X}}\gamma_t\langle \dot{X}\dot{X}\rangle + \gamma_r\langle \dot{\psi}\dot{\psi}\rangle\frac{\partial^2}{\partial \dot{\psi}} + \frac{\partial^2}{\partial \dot{\psi}\partial \dot{X}}(\gamma_{tr}\langle \dot{\psi}\dot{\psi}\rangle + \gamma_{rt}\langle \dot{X}\dot{X}\rangle)\right)\Bigg\} P_2. \end{aligned} \tag{A 8}$$

In the same way we obtain the Fokker–Planck equations of any multi-dimensional Langevin equation. Examples are equations (33) and (51) of the text.

Appendix B

Here we discuss in more detail the physical meaning of the off-diagonal terms of the ' friction ' matrix $\boldsymbol{\gamma}$.

Consider the simple form of rototranslational Langevin equation :

$$\dot{\mathbf{v}} = -\gamma_t \mathbf{v} - \gamma_{tr}\boldsymbol{\omega} + \tilde{\mathbf{f}}(t), \tag{B 1}$$

$$\dot{\boldsymbol{\omega}} = -\gamma_{rt}\mathbf{v} - \gamma_r \boldsymbol{\omega} + \tilde{\boldsymbol{\Gamma}}(t). \tag{B 2}$$

We may express (B 1) and (B 2) in terms of the linear velocity $\mathbf{v}$ as follows. By Laplace transformation :

$$-\mathbf{v}(0) + s\hat{\mathbf{v}} = -\gamma_t \hat{\mathbf{v}} - \gamma_{tr}\boldsymbol{\omega} + \hat{\mathbf{f}}, \tag{B 3}$$

$$-\boldsymbol{\omega}(0) + s\hat{\boldsymbol{\omega}} = -\gamma_r \hat{\boldsymbol{\omega}} - \gamma_{rt}\hat{\mathbf{v}} + \hat{\boldsymbol{\Gamma}}, \tag{B 4}$$

(with the notation : $\hat{g} \equiv \mathscr{L}[g(t)] \equiv \hat{g}(s)$), so that

$$-\mathbf{v}(0) + s\hat{\mathbf{v}} = \left(-\gamma_t + \frac{\gamma_{tr}\gamma_{tr}}{s+\gamma_r}\right)\hat{\mathbf{v}} + \hat{\mathbf{f}}'$$

$$\equiv -\hat{\beta}_v(s)\hat{\mathbf{v}} + \hat{\mathbf{f}}' \tag{B 5}$$

where

$$\hat{\mathbf{f}}' = \hat{\mathbf{f}} + \frac{(\hat{\boldsymbol{\Gamma}} + \boldsymbol{\omega}(0))}{s+\gamma_r} \tag{B 6}$$

We examine now the Laplace transform of the memory kernel $\hat{\beta}_v(s)$ in (B 5) in the case :

$$|\gamma_{tr}|,\ |\gamma_{rt}| \ll \gamma_r,\ \gamma_t.$$

We may approximate it with the Markovian assumption :

$$\hat{\beta}_v(s) = \gamma_t - \frac{\gamma_{rt}\gamma_{tr}}{s+\gamma_r} \doteq \gamma_t\left(1 - \frac{\gamma_{rt}\gamma_{tr}}{\gamma_r\gamma_t}\right) \tag{B 7}$$

A similar approach may be made to obtain

$$\hat{\beta}_\omega(s) \doteq \gamma_r\left(1 - \frac{\gamma_{rt}\gamma_{tr}}{\gamma_r\gamma_t}\right). \tag{B 8}$$

Equations (B 7) and (B 8) imply that in the presence of off-diagonal elements of $\boldsymbol{\gamma}$ translational and rotational frictions are diminished if γ_{rt} and γ_{tr} have the same signs. Otherwise the R/T interaction increases both the rotational and translational frictions separately considered.

It is preferable to call $\boldsymbol{\gamma}$ a dissipative matrix rather than a frictional matrix. It seems possible then that its off-diagonal elements may differ in sign. This is a question which must be settled with the aid of far infrared/microwave data and careful non-linear least mean squares multiparameter analysis using algorithms especially designed for this purpose.

Appendix C

In this Appendix we write down the explicit expression for the probability density function defined by equations (25) or (28). For the asymmetric top motion defined by (40) or (44) the solution is analytically tractable. It is given by :

$$p(\mathbf{A}(t);\ t|\mathbf{A}(0)) = (2\pi)^{-(n/2)}(\det V(t)^{-1/2})$$
$$\times \exp\left[-1/2(\mathbf{A}(t) - \mathbf{C}_\mathbf{A}(t)\mathbf{A}(0))^T \mathbf{V}^{-1}(t)(\mathbf{A}(t) - \mathbf{C}_\mathbf{A}(t)\mathbf{A}(0))\right],$$

where

$$\mathbf{V}(t) = \langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle - \mathbf{C}_\mathbf{A}(t)\langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle \mathbf{C}_\mathbf{A}{}^T(t),$$
$$\mathbf{C}_\mathbf{A}(t) = \langle \mathbf{A}(t)\mathbf{A}^T(0)\rangle \langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle^{-1}.$$

Define $\boldsymbol{\xi} = m\mathbf{v}$; $\boldsymbol{\Omega} = I\boldsymbol{\omega}$; then : $\mathbf{A} = \begin{bmatrix} \boldsymbol{\xi} \\ \boldsymbol{\Omega} \end{bmatrix}$;

$$p(\mathbf{A}(t);\ t|\mathbf{A}(0)) = \frac{(2\pi)^{-(n/2)}}{(A_0 D - BC)^{1/2}} \exp\left[-\tfrac{1}{2}\frac{x(Dx - By) + y(A_0 y - Cx)}{A_0 D - BC}\right], \tag{C 1}$$

$$A_0 = \langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(0)\rangle - \langle \boldsymbol{\xi}\boldsymbol{\xi}(0)\rangle\langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(0)\rangle^{-1}\langle \boldsymbol{\xi}\boldsymbol{\xi}(0)\rangle - \langle \boldsymbol{\xi}\boldsymbol{\Omega}(0)\rangle\langle \boldsymbol{\Omega}(0)\boldsymbol{\Omega}(0)\rangle^{-1}$$
$$\times \langle \boldsymbol{\xi}\boldsymbol{\Omega}(0)\rangle,$$

$$B = -\langle \boldsymbol{\xi}\boldsymbol{\xi}(0)\rangle\langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(0)\rangle^{-1}\langle \boldsymbol{\Omega}\boldsymbol{\xi}(0)\rangle - \langle \boldsymbol{\xi}\boldsymbol{\Omega}(0)\rangle\langle \boldsymbol{\Omega}(0)\boldsymbol{\Omega}(0)\rangle^{-1}\langle \boldsymbol{\Omega}\boldsymbol{\Omega}(0)\rangle,$$

$$C = -\langle \boldsymbol{\Omega}\boldsymbol{\xi}(0)\rangle\langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(0)\rangle^{-1}\langle \boldsymbol{\xi}\boldsymbol{\xi}(0)\rangle - \langle \boldsymbol{\Omega}\boldsymbol{\Omega}(0)\rangle\langle \boldsymbol{\Omega}(0)\boldsymbol{\Omega}(0)\rangle^{-1}\langle \boldsymbol{\xi}\boldsymbol{\Omega}(0)\rangle,$$

$$D = \langle \boldsymbol{\Omega}(0)\boldsymbol{\Omega}(0)\rangle - \langle \boldsymbol{\Omega}\boldsymbol{\xi}(0)\rangle\langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(0)\rangle^{-1}\langle \boldsymbol{\Omega}\boldsymbol{\xi}(0)\rangle - \langle \boldsymbol{\Omega}\boldsymbol{\Omega}(0)\rangle\langle \boldsymbol{\Omega}(0)\boldsymbol{\Omega}(0)\rangle^{-1}$$
$$\times \langle \boldsymbol{\Omega}\boldsymbol{\Omega}(0)\rangle,$$

$$x = \boldsymbol{\xi}(t) - \langle \boldsymbol{\xi}\boldsymbol{\xi}(0)\rangle\langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(0)\rangle^{-1}\,\boldsymbol{\xi}(0) - \langle \boldsymbol{\xi}\boldsymbol{\Omega}(0)\rangle\langle \boldsymbol{\Omega}(0)\boldsymbol{\Omega}(0)\rangle^{-1}\,\boldsymbol{\Omega}(0),$$

$$y = \boldsymbol{\Omega}(t) - \langle \boldsymbol{\Omega}\boldsymbol{\xi}(0)\rangle\langle \boldsymbol{\xi}(0)\boldsymbol{\xi}(0)\rangle^{-1}\,\boldsymbol{\xi}(0) - \langle \boldsymbol{\Omega}\boldsymbol{\Omega}(0)\rangle\langle \boldsymbol{\Omega}(0)\boldsymbol{\Omega}(0)\rangle^{-1}\,\boldsymbol{\Omega}(0).$$

In the Langevin model the angular and linear momentum correlation functions are given by expressions similar to (40), where the tensor products are replaced by scalar products.

Equation (46) defines the relevant autocorrelation functions for the itinerant oscillator/librator, and when these are used in (1) we have an analytical solution for (51). The consideration of such probability density functions is essential for the description of light scattering and neutron scattering spectra, which indirectly measure the molecular van Hove distribution function $G(\mathbf{R}, \mathbf{W}, \mathbf{W}', t)$, which is the probability of finding a molecule at $\mathbf{R}$ at time t with an orientation $\mathbf{W}$, given that a molecule (the same or another) was found at the origin (in the laboratory frame) at time $t = 0$ with an orientation $\mathbf{W}'$. A single particle theory such as in this paper may be used to calculate the self part of G, i.e. G_s. Importantly, there is no longer any reason why the orientational and coordinate parts of G_s should be considered separately, i.e. the rotation/translation coupling can be considered explicitly within the context of matrix Mori theory. The self structure factor, of prominent importance in radiation scattering theory, may be defined as :

$$F_s(k, t) = \exp\left[-\frac{k^2}{6}\langle|\Delta\mathbf{R}|^2\rangle\right] \tag{C 2}$$

within the context of the itinerant oscillator model, for example, where $\Delta\mathbf{R}$, the mean square displacement of the molecular centre of mass, may be calculated from :

$$\langle|\Delta\mathbf{R}|^2\rangle = 2\int_0^t (t-\tau)\langle\mathbf{V}(\tau)\,.\,\mathbf{V}(0)\rangle\,d\tau \qquad \text{(C 3)}$$

which may be calculated from (46) with full account of translation/rotation interaction. In (C 2) k is the momentum transfer.

Appendix D

The molecular van Hove self correlation function

The calculation of $G_s(\mathbf{R}, \mathbf{W}, \mathbf{W}', t)$ has been indirectly discussed for a general column vector $\mathbf{A}$ by Davies and Evans [14]. In this Appendix we evaluate it explicitly for $\mathbf{A} = \begin{bmatrix} \boldsymbol{\xi} \\ \boldsymbol{\Omega} \end{bmatrix}$ with the usual disc or planar itinerant oscillator model constraints. The first step is to write $\dot{\mathbf{A}}$ for $\mathbf{A}$ in equation (1) so that :

$$\ddot{\mathbf{A}}(t) = i\boldsymbol{\Omega}_{\mathbf{A}}\dot{\mathbf{A}}(t) - \int_0^t d\tau\,\phi_{\dot{\mathbf{A}}}(t-\tau)\dot{\mathbf{A}}(\tau) + \mathbf{F}_{\dot{\mathbf{A}}}(t). \qquad \text{(D 1)}$$

Equation (D 1) governs the behaviour of $\mathbf{A} = \begin{bmatrix} \mathbf{R} \\ \mathbf{W} \end{bmatrix}$. Here $\mathbf{R}$ is the position of the molecular centre of mass in the laboratory frame and $\mathbf{W}$ the molecular Euler orientation. If we restrict the reorientation to a plane then $\mathbf{W}$ reduces to a scalar θ. This facilitates the calculation considerably. The solution of (D 1) in this context (and, indeed, generally [14]) is :

$$\mathbf{A}(t) = \mathbf{A}(0) + \mathbf{X}_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0) + \int_0^t d\tau\,\mathbf{X}_{\dot{\mathbf{A}}}(t-\tau)\mathbf{F}_{\dot{\mathbf{A}}}(\tau), \qquad \text{(D 2)}$$

where $\mathbf{X}_{\dot{\mathbf{A}}}(t)$ is correlation matrix defined by :

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

$$(\dot{\mathbf{X}}_{\dot{\mathbf{A}}}(t) = \mathbf{C}_{\dot{\mathbf{A}}}(t)).$$

The self part of the molecular van Hove function is precisely the probability density function $p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0), \dot{\mathbf{A}}(0))$.

Explicitly :

$$\begin{aligned} &G_s(\mathbf{R}, \mathbf{W}, \mathbf{W}', t) \\ &\quad \equiv p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0), \dot{\mathbf{A}}(0)) \\ &\quad = (2\pi)^{-(n/2)}(\det \mathbf{W}(t))^{-1/2}\exp\,[-(1/2(\mathbf{A}(t) - \mathbf{A}(0) - \mathbf{X}_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))^T \\ &\qquad\qquad \times \mathbf{W}^{-1}(t)(\mathbf{A}(t) - \mathbf{A}(0) - \mathbf{X}_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))]. \end{aligned} \qquad \text{(D 3)}$$

The variance–covariance matrix is now :

$$\begin{aligned} \mathbf{W}(t) &= \langle(\mathbf{A}(t) - \mathbf{A}(0) - \mathbf{X}_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))(\mathbf{A}(t) - \mathbf{A}(0) - \mathbf{X}_{\dot{\mathbf{A}}}(t)\dot{\mathbf{A}}(0))^T\rangle \\ &= 2(\mathbf{1} - \mathbf{C}_{\mathbf{A}}(t))\langle\mathbf{A}(0)\mathbf{A}^T(0)\rangle - \mathbf{X}_{\dot{\mathbf{A}}}(t)\langle\dot{\mathbf{A}}(0)\dot{\mathbf{A}}^T(0)\rangle\mathbf{X}_{\dot{\mathbf{A}}}{}^T(t). \end{aligned}$$

If we restrict ourselves to the Langevin equations for disc rototranslation or for planar itinerant libration interacting with space oscillation we have :

$$\mathbf{A} = \begin{bmatrix} m\mathbf{R} \\ I\theta \end{bmatrix}; \quad \dot{\mathbf{A}} = \begin{bmatrix} \boldsymbol{\xi} \\ \Omega \end{bmatrix}, \quad \text{where} \quad \Omega \equiv I\dot{\theta}.$$

Equation (D 3) may be evaluated analytically using (40) or (46) given that :

$$\mathbf{X}_{\dot{\mathbf{A}}}(t) = -\dot{\mathbf{C}}_{\mathbf{A}}(t)\langle\mathbf{A}(0)\mathbf{A}^T(0)\rangle\langle\dot{\mathbf{A}}(0)\dot{\mathbf{A}}^T(0)\rangle^{-1}.$$

It is important to note that $\theta(t)$ of $\mathbf{A}$ in (D 3) is the *total* angle turned through in time t. The *angular orientation* is restricted to the range $-\pi \leqslant \theta \leqslant \pi$ and does not have a Gaussian but a wrapped-normal distribution, which in the decoupled limit may be approximated by von Mises distribution as discussed by Davies and Evans. The evaluation of $G(\mathbf{R}, \mathbf{W}, \mathbf{W}', t)$ in this context will be pursued numerically elsewhere.

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