Molecular rototranslation in condensed phases : single particle theory

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(*Received* 31 *May* 1979 ; *revision received* 6 *August* 1979)

A multidimensional expansion of the Mori equation in terms of a chain of Markov equations is used to develop a theory of molecular rototranslation in condensed phases. The stochastic equations of motion are solved for transient and equilibrium averages of the relevant dynamical variables. The single particle rototranslational Langevin equations correspond to the first equation of the Markov chain and (with a rotational constraint) are solved using Wiener matrix algebra for a possible sixteen autocorrelation functions. The Einstein result for the mean-square velocity and angular velocity is generalized. The third dimension of the Markov chain corresponds mechanically to the (constrained) rototranslation of a molecule bound to a cage of nearest neighbours by a dissipative matrix γ. The cage is itself undergoing a rototranslational Brownian motion. The problem of evaluating the formal theory with experimental measurements is discussed in terms of the number of parameters associated with each approximant (or dimensionality of the Markov chain). It is possible to avoid using a least-mean-squares fitting procedure by using a broad enough range of data and simulator results.

1. Introduction

In this paper we develop the formal theory of Markovian rototranslational, single particle, motion in condensed phases. With the aid of the matrix algebra of Wiener processes it is possible to establish in a few pages the averages of interest experimentally, starting from the simultaneous stochastic differential equations governing the motion. These include non-equilibrium averages such as the mean velocity, mean position, mean angular velocity, mean total angular displacement and their moments. The probability density functions and equilibrium autocorrelations follow in a straightforward manner. A formal development such as this is needed to begin the attempt at explaining analytically the recent results of molecular dynamics simulations, which indicate for N_2 symmetries a strong mutual effect of molecular translation at an arbitrary $t=0$ upon the rotation of the same molecule at time t later and *vice versa*. Single molecule Langevin equations are used to describe the rototranslation, representing the simplest approach to the problem, but even in this case the rotation of the asymmetric top must be fixed about a laboratory z-axis for the sake of mathematical tractability. This constraint is removed if we neglect inertial effects so that

0026-8976/80/3906 1391 $02·00

the equivalent of Perrin's equations may be extracted for rototranslation. We develop for rototranslation the treatises of Chandrasekhar [1] or Uhlenbeck *et al.* [2] and derive in § 2 a modification of Einstein's result [3] for the translational diffusion coefficient. This is observable directly in colloidal solutions. By considering Brownian rototranslation rather than translation, Perrin's estimate [4] of the Boltzmann constant is modified. Similarly the purely rotational single particle theory used in some types of light scattering from colloidal or polymer solutions is extended to rototranslation.

In § 1 the coupled single particle Langevin equations are derived as the first approximant of the Mori continued fraction expansion of the stochastic Liouville equation governing the Hilbert space evolution of dynamical column vectors. These are rewritten in a form amenable to solution using the statistics of Wiener processes [5]. Section 2 then elaborates the solution in terms of the quantities of interest (observable, for example, by computer simulation). Section 3 deals with the probability density functions which are the solution of the Fokker–Planck equations governing the system. Some of these are of course directly related to observables such as the structure factor and self part of the molecular van Hove self correlation function [6].

Section 2

The stochastic Liouville equation may be written with the use of projection operators in the form [8]

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

where $\mathbf{A}$ is a column vector of linearly independent dynamical variables, $\boldsymbol{\Omega}_{\mathbf{A}}$ a resonance frequency operator, $\phi_{\mathbf{A}}$ an effective liouvillian referred to as a memory matrix and $\mathbf{F}$ a projected force/torque vector. We have shown elsewhere [7, 9] that (1) may be written as

$$\frac{d}{dt}\mathbf{V} = i\boldsymbol{\omega} \,.\, \mathbf{V} - \boldsymbol{\alpha} \,.\, \mathbf{V} - \boldsymbol{\sigma} \,.\, \mathbf{V} + \boldsymbol{\Phi}(t). \tag{2}$$

Equation (2) represents a series of linked Markov equations, $\mathbf{V}$ is an n-dimensional column vector of m components which are in turn m-dimensional vectors. $\boldsymbol{\omega}$, $\boldsymbol{\alpha}$, $\boldsymbol{\sigma}$ and $\mathbf{F}$ are similarly structured and defined fully elsewhere [9]. Equation (2) represents a series of equations corresponding to the Mori continued fraction expansion of (1). The first approximant of this continued fraction is equivalent to

$$\dot{\mathbf{A}} = -\boldsymbol{\gamma} \,.\, \mathbf{A} + \mathbf{F}(t), \tag{3}$$

when the resonance operator is null (see appendix for a full discussion of symmetry). Equation (3) is the simplest approximation to the stochastic Liouville equation governing the dynamics of the vector $\mathbf{A}$. Equation (2) is a powerful, grand-matrix representation of the Mori equation, and rototranslational coupling is an example of its use. For single particle rototranslation we may write

$$\mathbf{A} = \begin{bmatrix} \mathbf{p} \\ \boldsymbol{\Omega} \end{bmatrix}, \tag{4}$$

where $\mathbf{p}$ is the linear momentum of the particle and $\boldsymbol{\Omega}$ its angular momentum. If the particle is an asymmetric top within which is embedded an axis of reference (e.g. a dipole axis) which we constrain to rotate about a fixed laboratory axis (z) then

$$\mathbf{A} = \begin{bmatrix} m\mathbf{v} \\ I\boldsymbol{\omega} \end{bmatrix}, \tag{5}$$

where m is the mass of the particle, $\mathbf{v}$ its centre of mass linear velocity, I its moment of inertia about the fixed axis and $\boldsymbol{\omega}$ its scalar angular velocity about this axis. At low frequencies we may approximate (3) by neglecting inertial effects

$$\dot{\mathbf{A}}_L + \boldsymbol{\gamma}_L \,.\, \mathbf{A}_L = \mathbf{F}_L(t). \tag{6}$$

Equation (6) is a representation of the Euler/Langevin equations [4] for Brownian motion of an asymmetric top which is both translating and rotating. Equation (6) may be solved without the rotational constraint imposed in (5) to give, for example, rototranslational Perrin equations (4) for the complex susceptibility. If we write the Liouville matrix $\boldsymbol{\gamma}$ in (3) as:

$$\boldsymbol{\gamma} = \begin{bmatrix} \lambda_{\mathrm{t}} & \lambda_{\mathrm{tr}} \\ \lambda_{\mathrm{rt}} & \lambda_{\mathrm{r}} \end{bmatrix} \tag{7}$$

then

$$m\dot{\mathbf{v}} = -\lambda_{\mathrm{t}} m\mathbf{v} - \lambda_{\mathrm{tr}} I\boldsymbol{\omega} + \mathbf{F}, \tag{8}$$

$$I\dot{\boldsymbol{\omega}} = -\lambda_{\mathrm{r}} I\boldsymbol{\omega} - \lambda_{\mathrm{rt}} m\mathbf{v} + \mathbf{T}, \tag{9}$$

which may be identified as simultaneous stochastic differential equations of the Langevin type and therefore as descriptive of Brownian motion. If $\lambda_{\mathrm{tr}} = \lambda_{\mathrm{rt}} = 0$, then (8) becomes the Langevin equation for translational Brownian motion and (9) describes a constrained rotational Brownian motion. By analogy $\boldsymbol{\gamma}$ is a friction matrix. The multi-particle equivalents of (8) and (9) have been considered recently by Wolynes and Deutch [10]. λ_{tr} represents the effect of rotational friction on centre of mass translation and λ_{rt} vice versa. A detailed discussion of the physical significance of $\boldsymbol{\gamma}$ is given elsewhere.

The rest of this section is devoted to solving (8) and (9) for averages of interest. These may be directly observable using a microscope (colloidal suspensions, pollen, etc.) or by light scattering [11] and dielectric spectroscopy [12]. Equations (8) and (9) are also approximations to the equations governing molecular rototranslation as observable by computer simulation [6]. Their solution is aided by the available matrix algebra of Wiener processes discussed by Coffey and co-workers [13, 14]. $\mathbf{F}$ and $\mathbf{T}$ are represented by Wiener processes $\dot{\mathbf{W}}_1$ and $\dot{\mathbf{W}}_2$ with considerable manipulative advantages such as

$$\langle (\mathbf{W}(t_1) \,.\, \mathbf{e}_1)(\mathbf{W}(t_2) \,.\, \mathbf{e}_2) \rangle = c^2 \min(t_1, t_2) \tag{10}$$

where $\mathbf{e}$ is a constant vector and c a constant to be determined. Without loss of generality the ith ($i = x, y, z$) component of equations of (8) and (9) may be considered for the purposes of calculation. One can then take the scalar relations

$$\left.\begin{aligned} W_i(t_2) - W_i(t_1) &= \xi_i(t_2 - t_1), \\ \langle \xi_i(\Delta) \rangle &= 0, \\ \langle \xi_i(\Delta)\xi_i(\Delta') \rangle &= c^2 |\Delta \cap \Delta'|, \end{aligned}\right\} \tag{11}$$

where Δ denotes a time difference and $|\ |$ the length of the interval $\Delta \cap \Delta'$. With these definitions the solution of equations (8) and (9) is that of the matrix equation

$$\dot{\mathbf{X}}(t) = \mathbf{A}\,\mathbf{X}(t) + \mathbf{B}\,\dot{\mathbf{W}}_i(t), \tag{12}$$

which is

$$\mathbf{X}(t) = \exp(\mathbf{A}t)\,\mathbf{X}(0) + \int_0^t \exp[\mathbf{A}(t-\tau)]\mathbf{B}\boldsymbol{\xi}(d\tau), \tag{13}$$

where $\mathbf{X}(0)$ is the initial value of the matrix $\mathbf{X}(t)$.

The maximum information may be extracted from equation (8) and (9) if they are identified with $\mathbf{X}$, $\mathbf{A}$ and $\dot{\mathbf{W}}_i$ as follows :

$$\mathbf{X} = \begin{bmatrix} \theta \\ R \\ \omega \\ v \end{bmatrix}; \quad \mathbf{A} = \begin{bmatrix} 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \\ 0 & 0 & -\lambda_r & -\lambda_{rt}^* \\ 0 & 0 & -\lambda_{tr}^* & -\lambda_t \end{bmatrix}, \tag{14}$$

$$\mathbf{B} = \begin{bmatrix} 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 1 & 0 \\ 0 & 0 & 0 & 1 \end{bmatrix}; \quad \dot{\mathbf{W}} = \begin{bmatrix} 0 \\ 0 \\ \mathbf{W}_3 \\ \mathbf{W}_4 \end{bmatrix}, \tag{15}$$

Here $\lambda_{rt}^* = \lambda_{rt}(m/I)$; $\lambda_{tr}^* = (I/m)\lambda_{tr}$; θ denotes the *total* angle through which the molecule has rotated since the arbitrary $t = 0$; and R a component of the centre of mass position vector.

With these definitions, it is convenient to use the Laplace transform

$$\tilde{\mathbf{X}}(s) = \mathscr{L}[\mathbf{X}(t)] = \int_0^\infty \exp(-st)\,\mathbf{X}(t)dt, \tag{16}$$

so that

$$\mathscr{L}^{-1}[(s\mathbf{1} - \mathbf{A})^{-1}] = \exp(\mathbf{A}t), \tag{17}$$

$$\mathscr{L}^{-1}[(s\mathbf{1} - \mathbf{A})^{-1}\,\mathbf{B}\boldsymbol{\xi}] = \int_0^t \exp[\mathbf{A}(t-\tau)]\mathbf{B}\boldsymbol{\xi}(d\tau), \tag{18}$$

$$\langle \mathbf{X}(t) \rangle = \exp(At)\,\mathbf{X}_0, \tag{19}$$

$$\mathbf{Y}(t) = \mathbf{X}(t) - \langle \mathbf{X}(t) \rangle = \int_0^t \exp[\mathbf{A}(t-\tau)]\mathbf{B}\boldsymbol{\xi}(d\tau). \tag{20}$$

In equations (19) and (20) $\langle\ \rangle$ denotes a non-equilibrium (transient) time average. Note that in some cases, at equilibrium :

$$\langle \mathbf{X}(t) \rangle \xrightarrow[t\to\infty]{} \mathbf{0}.$$

It is possible therefore to obtain expressions for the non-equilibrium averages of θ, R, ω, and v, for their moments and mixed moments. Further analytical averaging is then possible for the purposes of comparison with observables, as described in Chandrasekhar's [1] equations (214) to (217). The influence of rotation on, for example, the mean-square displacement may then be given analytical form in terms of λ_t, λ_r, λ_{tr}^* and λ_{rt}^*. Some of these variables are evaluated explicitly in § 2.

Section 3

The matrix $\exp(\mathbf{A}t)$ is the inverse Laplace transform of :

$$(s\mathbf{1} - \mathbf{A})^{-1} = \begin{bmatrix} s[(s+\lambda_r)(s+\lambda_t) - \lambda_{rt}^*\lambda_{tr}^*]; & 0 ; & s(s+\lambda_t) ; & -\lambda_{rt}^* s \\ 0 ; & s[(s+\lambda_r)(s+\lambda_t) - \lambda_{rt}^*\lambda_{tr}^*]; & -\lambda_{tr}^* s ; & (s+\lambda_r)s \\ 0 ; & 0 ; & s^2(s+\lambda_t) ; & -\lambda_{rt}^* s^2 \\ 0 ; & 0 ; & -\lambda_{tr}^* s^2 ; & -(s+\lambda_r)s^2 \end{bmatrix} \times [s^2((s+\lambda_t)(s+\lambda_r) - \lambda_{tr}^*\lambda_{rt}^*)]^{-1}. \tag{21}$$

Denoting the elements of equation (21) by $\alpha_{ij}(t)$ (see the table), we may write down the averages :

$$\langle \theta(t) \rangle = \alpha_{11}(t)\theta(0) + \alpha_{13}(t)\omega(0) + \alpha_{14}(t)v(0), \tag{22}$$

$$\langle R(t) \rangle = \alpha_{22}(t)R(0) + \alpha_{23}(t)\omega(0) + \alpha_{21}(t)v(0), \tag{23}$$

$$\langle \omega(t) \rangle = \alpha_{33}(t)\omega(0) + \alpha_{34}(t)v(0), \tag{24}$$

$$\langle v(t) \rangle = \alpha_{43}(t)\omega(0) + \alpha_{44}(t)v(0). \tag{25}$$

Equations (22)–(25) are average values at time t *given* $\theta(0)$, $R(0)$, $\omega(0)$ or $v(0)$.

Note that the elements of the table may be identified with the following autocorrelation functions at equilibrium

$$\alpha_{11} = \langle \theta(t)\theta(0) \rangle / \langle \theta(0)\theta(0) \rangle ; \quad \alpha_{12} = \langle \theta(t)R(0) \rangle / \langle R(0)R(0) \rangle ;$$
$$\alpha_{13} = \langle \theta(t)\omega(0) \rangle / \langle \omega(0)\omega(0) \rangle ; \quad \alpha_{14} = \langle \theta(t)v(0) \rangle / \langle v(0)v(0) \rangle ;$$
$$\alpha_{21} = \langle R(t)\theta(0) \rangle / \langle \theta(0)\theta(0) \rangle ; \quad \alpha_{22} = \langle R(t)R(0) \rangle / \langle R(0)R(0) \rangle ;$$
$$\alpha_{23} = \langle R(t)\omega(0) \rangle / \langle \omega(0)\omega(0) \rangle ; \quad \alpha_{24} = \langle R(t)v(0) \rangle / \langle v(0)v(0) \rangle ;$$
$$\alpha_{31} = \langle \omega(t)\theta(0) \rangle / \langle \theta(0)\theta(0) \rangle ; \quad \alpha_{32} = \langle \omega(t)R(0) \rangle / \langle R(0)R(0) \rangle ;$$
$$\alpha_{33} = \langle \omega(t)\omega(0) \rangle / \langle \omega(0)\omega(0) \rangle ; \quad \alpha_{34} = \langle \omega(t)v(0) \rangle / \langle v(0)v(0) \rangle ;$$
$$\alpha_{41} = \langle v(t)\theta(0) \rangle / \langle \theta(0)\theta(0) \rangle ; \quad \alpha_{42} = \langle v(t)R(0) \rangle / \langle R(0)R(0) \rangle ;$$
$$\alpha_{43} = \langle v(t)\omega(0) \rangle / \langle \omega(0)\omega(0) \rangle ; \quad \alpha_{44} = \langle v(t)v(0) \rangle / \langle v(0)v(0) \rangle .$$

All sixteen of these autocorrelation functions can be simulated by computer. There is enough scope therefore to evaluate λ_t, λ_r and λ_{rt}^* λ_{tr}^* with or without the use of non-linear least-mean-squares fitting. The apparent contradiction in the table between element (4, 1) and (1, 4) or (3, 1) and (1, 3) arises from the fact

Row	Column 1	2	3	4
1	1	0	$\frac{[yx+b+\exp(-bt)[(x-yb)\sin xt-(yx+b)\cos xt]]}{(x^2+b^2)}$	$\lambda_{rt}^*\frac{(\exp(-bt)(b\sin xt+x\cos xt)-x)}{(x^2+b^2)}$
2	0	1	$\lambda_{tt}^*\frac{(\exp(-bt)(b\sin xt+x\cos xt)-x)}{(x^2+b^2)}$	$-\frac{\lambda_{rt}^*}{2}\left[\frac{(\exp[-(b+x)t]-1)}{b+x}-\frac{(\exp[-(b-x)t]-1)}{b-x}\right]$
3	0	0	$\exp(-bt)(\cos xt+y\sin xt)$	$-{}^*\lambda_{rr}\exp(-bt)\sin xt$
4	0	0	$-{}^*\lambda_{tr}\exp(-bt)\sin xt$	$\exp(-bt)(\cos xt+y_1\sin xt)$

Row	Column 1	2	3	4
1	1	0	$\left[\frac{(1+y)}{(x-b)}(\exp[(x-b)t]-1)-(1-y)(\exp[-(x+b)t]-1)\right]$	$[y_1x+b+\exp(-bt)[(x-y_1b)\sin xt-(y_1x+b)\cos xt]]$
2	0	1	$-\lambda_{tt}^*\left[\frac{(\exp[-(b+x)t]-1)}{b+x}-\frac{(\exp[-(b-x)t]-1)}{b-x}\right]$	$-\frac{\lambda_{rt}^*}{2}\left[\frac{(1+y_1)}{(x-b)}(\exp[(x-b)t]-1)-\frac{(1-y_1)}{(x+b)}(\exp[-(x+b)t]-1)\right]$
3	0	0	$\exp(-bt)(\cos xt+y\sin xt)$	$-{}^*\lambda_{rr}\exp(-bt)\sin xt$
4	0	0	$-{}^*\lambda_{tr}\exp(-bt)\sin xt$	$\exp(-bt)(\cosh xt+y_1\sinh xt)$

that ((24) and (25)) there is no means of directly calculating the relation between $v(t)$ and $\theta(0)$, for example, but that between $\theta(t)$ and $v(0)$ is given by an equation such as (22). The result is that $\langle v(t)\theta(0)\rangle/\langle\theta(0)\theta(0)\rangle$ is indeterminate by reference to element α_{41}, which is set to zero. However, there is, of course, a straightforward general relation between $\langle v(t)\theta(0)\rangle$ and $\langle\theta(0)v(t)\rangle$.

Another apparently strange result is that

$$\langle R(t)R(0)\rangle/\langle R(0)R(0)\rangle = 1,$$

$$\langle\theta(t)\theta(0)\rangle/\langle\theta(0)\theta(0)\rangle = 1.$$

However, these may be easily checked by solving directly the relevant Langevin equation in the absence of rotation/translation interaction, when the same result is obtained. For example, if we take Laplace transforms of :

$$\ddot{R}(t) = -\lambda(t)\dot{R}(t) + F(t)/m\ ;$$

i.e.

$$\bar{R}(s) = \frac{R(0)}{s} + \frac{\dot{R}(0) + [F(t)/m]}{s(s+\lambda^{(v)})},$$

then clearly on taking the inverse and constructing $\langle R(t)R(0)\rangle$, the above result is recovered. It is a consequence of the fact that the second moment of the velocity autocorrelation function is infinite [15], implying that the first moment of the position autocorrelation function is, in turn, infinite.

This restriction is removed by taking higher approximants of (1), or equivalently, increasing η in (2).

3.1. *The mean displacement and its moments*

The mean-square displacement of rototranslating pollen particles after the arbitrary $t = 0$ is directly observable along an x, y or z axis of the laboratory frame. This may be estimated from (3) and (9) as follows. We first note the result

$$\langle(\mathbf{W}_i(t_1)\cdot\mathbf{e})(\mathbf{W}_j(t_1)\cdot\mathbf{e})\rangle = 0, \tag{26}$$

when i and j are not identical. From (13) we have

$$v(t) = \alpha_{33}(t)v(0) + \alpha_{34}(t)v(0) + \int_0^t \alpha_{43}(t-\tau)\xi_3(d\tau) + \int_0^t \alpha_{44}(t-\tau)\xi_4(d\tau), \tag{27}$$

so that the displacement of the centre of mass is

$$R(t) - R(0) = \int_0^t v(t)\,dt. \tag{28}$$

The mean square of

$$R(t) - R(0) - \int_0^t \alpha_{43}(t)\omega(0)\,dt - \int_0^t \alpha_{44}(t)v(0)\,dt \tag{29}$$

is governed therefore by

$$C_3^2\int_0^t\left[\int_0^{t-\tau}\alpha_{33}(u)\,du\right]^2 d\tau + C_4^2\int_0^t\left[\int_0^{t-\tau}\alpha_{44}(u)du\right]^2 d\tau + C_3C_4\int_0^t\left[\int_0^{t-\tau}\alpha_{43}(u)\alpha_{44}(u)\,du\right]^2 d\tau, \tag{30}$$

where C_3^2 and C_4^2 are determined as below. The mean displacement of a particle undergoing rototranslational brownian motion according to (8) and (9) is then, in one dimension

$$\langle R(t)-R(0)\rangle = \int_0^t \alpha_{43}(t)\omega(0)\,dt + \int_0^t \alpha_{44}(t)v(0)\,dt, \tag{31}$$

while squaring (30) and averaging over the initial $v(0)$ and $\omega(0)$ gives us the equilibrium, observable, mean-square displacement in one dimension as

$$\ll(R(t)-R(0))\gg = \frac{kT}{m}\left[\frac{(1+y)}{(b-x)^2}(b-x)t+\exp(-(b-x)t)-1\right.$$
$$\left.+\frac{(1-y)}{(b+x)^2}((b+x)t+\exp(-(b+x)t)-1)\right], \tag{32}$$

where

$$y=\frac{\lambda_r-b}{(b^2-c)^{1/2}}; \quad x=(b^2-c)^{1/2};$$
$$b=2(\lambda_t+\lambda_r); \quad c=\lambda_t\lambda_r-\lambda_{tr}^*\,\lambda_{rt}^*.$$

As $t\to\infty$ we recover the rototranslational equivalent of Einstein's result of 1905

$$\ll(R(t)-R(0))^2\gg \xrightarrow[t\to\infty]{} \frac{2kTt}{m}\left(\frac{\lambda_r}{\lambda_t\lambda_r-\lambda_{tr}^*\,\lambda_{rt}^*}\right) \tag{33}$$

(in one dimension).

We note that

$$\frac{\lambda_r}{\lambda_t\lambda_r-\lambda_{tr}^*\,\lambda_{rt}^*}\to\frac{1}{\lambda_t}$$

in the decoupled limit, producing Einstein's relation used by Perrin to determine Boltzmann's constant from colloidal solutions.

Similarly

$$\ll(\theta(t)-\theta(0))^2\gg \xrightarrow[t\to\infty]{} \frac{2kTt}{I}\left(\frac{\lambda_t}{\lambda_t\lambda_r-\lambda_{tr}^*\,\lambda_{rt}^*}\right). \tag{34}$$

It would be more rigorous to calculate (33) and (34) from (6), removing the restriction on space rotation imposed above. By simulating the left-hand sides of (33) and (34) and higher moments it is possible to extract estimates of λ_t, λ_r, and $\lambda_{tr}^*\,\lambda_{rt}^*$. The analytical evaluation of moments of the squared displacement is considered below.

Equations (33) and (34) imply that

$$\lambda_t\lambda_r \geqslant \lambda_{tr}^*\,\lambda_{rt}^*$$

and also the interesting result that

$$\frac{\ll(R(t)-R(0))^2\gg}{\ll(\theta(t)-\theta(0))^2\gg}=\frac{I}{m}\frac{\lambda_r}{\lambda_t} \tag{35}$$

for finite rototranslational coupling, while in its absence the right-hand side of (35) is $(I/m)(\lambda_t/\lambda_r)$. This will serve as a simple test for such interaction when considering the results of computer simulations, using the apparent λ_t and λ_r

(derived from exponential $\langle \mathbf{v}(t)\,.\,\mathbf{v}(0)\rangle$ and $\langle\omega(t)\omega(0)\rangle$) or equivalently from the Einstein limits of (33) and (34).

In the case $c>b^2$ the result may be expressed as

$$\ll(R(t)-R(0))^2\gg$$
$$=\frac{2kT}{m}\left(\left[t-\frac{(b+xy)}{x^2+b^2}\right]\left[\exp(-bt)\frac{(x\sin xt-b\cos xt)}{x^2-b^2}+\frac{b}{x^2+b^2}\right]\right.$$
$$-\left[yt-\frac{(yb-x)}{x^2-b^2}\right]\left[\exp(-bt)\frac{(b\sin xt+x\cos xt)}{x^2+b^2}-\frac{x}{x^2+b^2}\right]$$
$$\left.+t\exp(-bt)\left[\frac{(yb-x)\sin xt+(yx+b)\cos xt}{x^2+b^2}\right]\right), \tag{36}$$

with

$$y=\frac{\lambda_r-b}{(c-b^2)^{1/2}}; \quad x=(c-b^2)^{1/2}.$$

Again, as $t\to\infty$ we recover the relations (33)–(35).

3.2. *The mean square linear and angular velocities*

These are regularly monitored at equilibrium in a molecular dynamics experiment and are expressed in terms of the variance and average of the probability density function. We have

$$\langle(\omega(t)-\langle\omega(t)\rangle)^2\rangle=\left\langle\left(\int_0^t \alpha_{33}(t-\tau)\xi_3(d\tau)+\int_0^t \alpha_{34}(t-\tau)\xi_4(d\tau)\right)^2\right\rangle, \tag{37}$$

$$\langle(v(t)-\langle v(t)\rangle)^2\rangle=\left\langle\left(\int_0^t \alpha_{43}(t-\tau)\xi_3(d\tau)+\int_0^t \alpha_{44}(t-\tau)\xi_4(d\tau)\right)^2\right\rangle. \tag{38}$$

Using again the properties of Wiener integrals we have:

$$\langle(\omega(t)-\langle\omega(t)\rangle)^2\rangle=C_3^2\,I_{33}+2C_3C_4I_{33,34}+C_4^2\,I_{34} \tag{39}$$
$$\xrightarrow[t\to\infty]{}\frac{kT}{I},$$

$$\langle(v(t)-\langle v(t)\rangle)^2\rangle=C_3^2\,I_{43}+2C_3C_4I_{43,44}+C_4^2\,I_{44}$$
$$\xrightarrow[t\to\infty]{}\frac{kT}{m}, \tag{40}$$

$$\langle(\omega(t)-\langle\omega(t)\rangle)(v(t)-\langle v(t)\rangle)\rangle$$
$$=C_3^2\,I_{33,43}+C_4^2\,I_{34,44}+C_3C_4(I_{33,44}+I_{34,43})$$
$$\xrightarrow[t\to\infty]{}0. \tag{41}$$

Here C_3 and C_4 are determined in the equilibrium limit ($t\to\infty$) for the equipartition theorem.

The integrals I are defined as

$$\left.\begin{aligned} I_{33} &= \int_0^t \alpha_{33}^2(t-\tau)\,d\tau\,; \quad I_{44} = \int_0^t \alpha_{44}^2(t-\tau)\,d\tau\,; \\ I_{34} &= \int_0^t \alpha_{34}^2(t-\tau)\,d\tau\,; \quad I_{43} = \int_0^t \alpha_{43}^2(t-\tau)\,d\tau\,; \\ I_{43,44} &= \int_0^t \alpha_{43}(t-\tau)\alpha_{44}(t-\tau)\,d\tau\,; \end{aligned}\right\} \tag{42}$$

etc. in an obvious way.

Solving in the $t\to\infty$ limit yields

$$C_3^2 = \frac{BC_1 + B_1C}{AB_1 - A_1B}\,; \quad C_4^2 = \frac{C - AC_3^2}{B}\,; \tag{43}$$

where (with $t\to\infty$)

$$\left.\begin{aligned} A &= I_{43} - \frac{I_{43,44}}{I_{33,34}}\,I_{33}\,; \quad B = I_{44} - \frac{I_{43,44}}{I_{33,34}}\,I_{34}\,; \\ C &= \frac{kT}{m} - \frac{I_{43,44}}{I_{33,34}}\,\frac{kT}{I}\,; \quad A_1 = I_{33,43} - \frac{(I_{33,44} + I_{34,43})}{2I_{33,34}}\,I_{33}\,; \\ B_1 &= I_{34,44} - \frac{(I_{33,44} + I_{34,43})}{2I_{33,34}}\,I_{34}\,; \\ C_1 &= \frac{(I_{33,44} + I_{34,43})}{2I_{33,34}}\,\frac{kT}{I}. \end{aligned}\right\} \tag{44}$$

These relations are sufficient to define analytically the probability density functions of velocity and angular velocity in terms of λ_t, λ_r and $\lambda_{tr}{}^*$ $\lambda_{rt}{}^*$.

3.3. *Bivariate p.d.f. of velocity and angular velocity*

In this case we are seeking the probability density function of both linear and angular velocity, which may be related in a simple manner to the van Hove self correlation function for mixed translational and space position. The Fokker–Planck equation corresponding to (1) has a Gaussian solution [16]

$$p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0)) = (2\pi)^{-(1/2)n}(\det \mathbf{v}(t))^{-1/2} \times \exp\left[-\tfrac{1}{2}(\mathbf{A}(t) - C_{\mathbf{A}}(t)\mathbf{A}(0))^T\mathbf{v}^{-1}(t)(\mathbf{A}(t) - C_{\mathbf{A}}(t)\mathbf{A}(0))\right], \tag{45}$$

with variance–covariance matrix:

$$\mathbf{v}(t) = \langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle - C_{\mathbf{A}}(t)\langle \mathbf{A}(0)\mathbf{A}^T(0)\rangle C_{\mathbf{A}}{}^T(t). \tag{46}$$

If the linear and angular velocities are statistically independent, then the equation above would factorize. This difference could be detected in a molecular dynamics simulation. Similarly, the habitual factorization [6] of the self van Hove function into spatial and angular parts could be avoided by evaluating in the Markov limit (equation (3)) the Mori equation (1) written as

$$\ddot{\mathbf{A}}(t) = i\Omega_{\dot{\mathbf{A}}}\dot{\mathbf{A}}(t) - \int_0^t \phi_{\dot{\mathbf{A}}}(t-\tau)\dot{\mathbf{A}}(\tau)d\tau + \mathbf{F}_{\dot{\mathbf{A}}}(t), \tag{47}$$

with

$$\mathbf{A} = \begin{bmatrix} \theta(t) \\ R(t) \end{bmatrix}$$

in the case of planar-constrained rototranslation described in this paper. The bivariate p.d.f. $p(\mathbf{A}(t)\,;\ t|\mathbf{A}(0))$ of velocity and angular velocity is naturally endowed with the property that knowledge of the variance–covariance matrix implies knowledge of all the higher moments through the usual moment generating function. In view of the tedious algebraic complexity associated with the analytical form of $\langle(v(t) - \langle v(t)\rangle)^2\rangle$, for example, these p.d.f.s are most easily evaluated numerically using the usual Hermite polynomial basis set and diagonalizing in the standard way. The comparison with the results of computer simulations will be possible with suitably designed fitting procedures for λ_t, λ_r, and $\lambda_{tr}{}^*$ $\lambda_{rt}{}^*$. Comparison of three or more such moments with their simulated equivalents would be sufficient to evaluate λ_t, λ_r and $\lambda_{tr}{}^*$ $\lambda_{rt}{}^*$ separately.

3.4. *Rototranslational motion of the inertialess asymmetric top*

In this case the space rototranslation of the asymmetric top may be evaluated analytically in the Markov limit using the approach of Perrin, more recently generalized by Favro [17]. The rototranslational Brownian motions of the colloidal or polymeric particles can be observed microscopically and at *low frequency* by an increasingly wide range of radiative methods such as neutron and light scattering and dielectric spectroscopy (if the particles are dipolar). In this case also it is relatively straightforward to link the single particle and multiparticle correlation functions with a suitable macro–micro correlation theorem [18]. The fundamental single particle equations may be written as

$$m\dot{\mathbf{v}} + m\mathbf{v}\boldsymbol{\lambda}_t + \mathbf{I}\boldsymbol{\Omega}\boldsymbol{\lambda}_{tr} = \mathbf{F}, \tag{48}$$

$$\mathbf{I}\dot{\boldsymbol{\Omega}} + \mathbf{I}\boldsymbol{\Omega}\boldsymbol{\lambda}_r + m\mathbf{v}\boldsymbol{\lambda}_{rt} = \mathbf{T}. \tag{49}$$

The functions $\boldsymbol{\lambda}_t$, $\boldsymbol{\lambda}_r$, $\boldsymbol{\lambda}_{tr}$ and $\boldsymbol{\lambda}_{rt}$ are now matrices which are assumed diagonal.

It is important to note that the Mori equation (1) is *not* tractable when dealing with asymmetric top space (three-dimensional) rototranslation in the non-Markov regime, but the multidimensional representation (equation 2) may be used to solve this problem straightforwardly, because the abstraction introduced by the use of projection operators is removed [7]. This is in spite of the fact that equation (1) and (2) are *fully equivalent*.

Section 4

The method of Wiener matrix algebra may be generalized to the non-Markov regime by expanding equation (2) as

$$\left.\begin{aligned} \dot{\mathbf{A}}_1 &= -\boldsymbol{\omega}_{12}\mathbf{A}_2 - \boldsymbol{\gamma}\mathbf{A}_1 + \mathbf{F}(t), \\ \dot{\mathbf{A}}_2 &= -\boldsymbol{\omega}_{21}\mathbf{A}_1 - \boldsymbol{\omega}_{23}\mathbf{A}_3, \\ \dot{\mathbf{A}}_3 &= -\boldsymbol{\omega}_{32}\mathbf{A}_2 - \boldsymbol{\omega}_{34}\mathbf{A}_4, \\ &\vdots \\ \mathbf{A}_{n+1} &= \mathbf{0}. \end{aligned}\right\} \tag{50}$$

$$\dot{\mathbf{X}}_0(t) = \mathbf{A}_0 \mathbf{X}_0(t) + B_0 \mathbf{W}(t), \tag{51}$$

where

$$A_0 = \begin{bmatrix}
0 & 0 & 0 & 0 & 1 & 0 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 1 & 0 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 1 & 0 \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 1 \\
-\Delta_2^{(t)2} & \Delta_2^{(t)2} & 0 & 0 & 0 & 0 & 0 & 0 \\
\Delta_1^{(t)2} & -\Delta_1^{(t)2} & 0 & 0 & 0 & -\gamma^{(t)} & 0 & \dfrac{-\Delta_2^{(r)}\Delta_1^{(t)}\gamma^{(tr)}}{\Delta_1^{(r)}\Delta_2^{(t)}} \\
0 & 0 & -\Delta_2^{(r)2} & \Delta_2^{(r)2} & 0 & 0 & 0 & 0 \\
0 & 0 & \Delta_1^{(r)2} & -\Delta_1^{(r)2} & 0 & \dfrac{-\Delta_2^{(t)}\Delta_1^{(r)}\gamma^{(rt)}}{\Delta_2^{(r)}\Delta_1^{(t)}} & 0 & -\gamma^{(r)}
\end{bmatrix} \tag{52}$$

$$\mathbf{X}_0(t) = \begin{bmatrix} X(t) \\ x(t) \\ \theta(t) \\ \psi(t) \\ \dot{X}(t) \\ \dot{x}(t) \\ \dot{\theta}(t) \\ \dot{\psi}(t) \end{bmatrix}; \quad \mathbf{W}_0(t) = \begin{bmatrix} 0 \\ 0 \\ 0 \\ 0 \\ 0 \\ W_1(t) \\ 0 \\ W_2(t) \end{bmatrix};$$

and B is an 8×8 matrix which is null except for the (6, 6) and (8, 8) elements, which are 1. In these matrices x is a component of the centre of mass of the itinerant oscillator cage, X of the encaged molecule and θ and ψ similarly define the planar angular motion of the system. $\Delta_2^{(t)2}$ is the mean square linear force of the encaged molecule, $\Delta_2^{(r)2}$ its angular counterpart. $\Delta_1^{(t)2}$ and $\Delta_1^{(r)2}$ are, similarly, equilibrium averages involving the mean square force (or torque) and its derivative. $\gamma^{(t)}$, $\gamma^{(r)}$, $\gamma^{(tr)}$ and $\gamma^{(rt)}$ are the elements of the matrix $\boldsymbol{\gamma}$ of (2). Obviously it is advisable to solve (51) numerically, but the analytically form of the associated secular equation is of interest since it tells us something about the physical nature of the model we have constructed. This is the determinantal

$$+ s((s+\gamma^{(t)})\Delta_2^{(t)2}\Delta_1^{(r)2} + (s+\gamma^{(r)})\Delta_1^{(t)2}\Delta_2^{(r)2}) + s^3(\Delta_1^{(r)2}(s+\gamma^{(t)}) + \Delta_1^{(t)2}(s+\gamma^{(r)}))] = 0. \tag{53}$$

We note that we obtain the (known) equations governing the purely translational itinerant oscillator or purely rotational planar itinerant librator, i.e. :

$$s^4[s^3 + s^2\gamma^{(t)} + s(\Delta_1^{(t)2} + \Delta_2^{(t)2}) + \Delta_2^{(t)2}\gamma^{(t)}](s+\gamma^{(r)}) = 0, \tag{54}$$

$$s^4[s^3 + s^2\gamma^{(r)} + s(\Delta_1^{(r)2} + \Delta_2^{(r)2}) + \Delta_2^{(r)2}\gamma^{(r)}](s+\gamma^{(t)}) = 0, \tag{55}$$

if the following associated conditions are obeyed.

(*a*) For (54): $\Delta_1^{(r)2} = \Delta_2^{(r)2} = 0$; $\gamma^{(tr)}\gamma^{(rt)} = 0$,

(*b*) For (55): $\Delta_1^{(t)2} = \Delta_2^{(t)2} = 0$; $\gamma^{(tr)}\gamma^{(rt)} = 0$.

We are now in a position to extract some physical information about rotation/translation in the non-Markov regions. This may be summarized as follows :

(i) the only natural instance of mutually exclusive translational or rotational motion occurs when rotation and translation (respectively) is absent. This is expected to be the case also for three-dimensional rototranslation and is *of course* expected on intuitive grounds ;

(ii) taking note of the structure within the [ ] brackets of (54) and (55) allows us to identify the factors γ_r, γ_t, γ_{rt} and γ_{tr} in terms of the model. These may be defined as follows.
γ_r = purely rotational part of the dissipative frequency matrix of the central molecule relative to a stationary cage,
γ_t = purely translation part of the dissipative frequency matrix of the central molecule relative to a stationary cage,
$\left.\begin{matrix}\gamma_{rt} = \\ \gamma_{tr} = \end{matrix}\right\}$ off diagonal elements of the frequency matrix ;

(iii) the truncated form of (1) resulting in (53), (54) and (55) is fully consistent with equations of motion which are *separately* Markovian (i.e. represented in (51)). The *truncated* Mori continued fraction is therefore *fully consistent* with the physical model of constrained itinerant oscillation/-libration ;

(iv) it is self-consistent to use a dissipative matrix of the form :

$$\begin{bmatrix} \gamma_t & \gamma_{tr} \\ \gamma_{rt} & \gamma_r \end{bmatrix}.$$

Physically, however, the motion of the molecule/cage system depends only on the *product* $\gamma_{tr}\gamma_{rt}$, so that individually their sign is irrelevant provided it is the same for γ_{rt} and γ_{tr}.

The transient mean-square linear velocity of the encaged molecule is taken from the (5, 5) element of $(1s-\mathbf{A}_0)^{-1}$. This is :

$$\tilde{F}^{(t)}(s)=\{s[s^2+\Delta_2{}^{(r)2}][(s+\gamma^{(t)})(s+\gamma^{(r)})-\gamma^{(rt)}\gamma^{(tr)}] +s^2[\Delta_1{}^{(t)2}(s+\gamma^{(r)})+\Delta_1{}^{(r)2}(s+\gamma^{(t)})] +\Delta_1{}^{(t)2}(s\Delta_1{}^{(r)2}+(s+\gamma^{(r)})\Delta_2{}^{(r)2})\}/\tilde{G}(s), \quad (56)$$

which in the decoupled limit reduces to :

$$\tilde{F}^{(t)}(s)=\frac{s^2+\gamma^{(t)}s+\Delta_1{}^{(t)2}}{s^3+\gamma^{(t)}s^2+(\Delta_1{}^{(t)2}+\Delta_2{}^{(t)2})s+\Delta_2{}^{(t)2}\,\gamma^{(t)}}, \quad (57)$$

which is exactly the expression derived by Coffey *et al.* [14] for the purely translational itinerant oscillator.

Similarly the transient mean-square angular velocity may be calculated using the function

$$\tilde{F}^{(r)}(s)=\{s[s^2+\Delta_2{}^{(t)2}][(s+\gamma^{(r)})(s+\gamma^{(t)})-\gamma^{(tr)}\gamma^{(rt)}] +s^2[\Delta_1{}^{(r)2}(s+\gamma^{(t)})+\Delta_1{}^{(t)2}(s+\gamma^{(r)})] +\Delta_1{}^{(r)2}(s\Delta_1{}^{(t)2}+(s+\gamma^{(t)})\Delta_2{}^{(t)2})\}/\tilde{G}(s), \quad (58)$$

which again reduces to an equation [13] similar to (57) in the decoupled limit.

Denoting the inverse Laplace transform of $\tilde{F}^{(t)}(s)$ by $F^{(t)}(t)$, then the mean-square linear displacement of the encaged particle is, in three-dimensions

$$\langle|\mathbf{R}(t)-\mathbf{R}(0)|^2\rangle=\exp\left[-\frac{6kT}{m}\int_0^t(t-\tau)F^{(t)}(\tau)\,d\tau\right] \quad (59)$$

and similarly (in two-dimensions)

$$\langle(\theta(t)-\theta(0))^2\rangle=\exp\left[-\frac{2kT}{I}\int_0^t(t-\tau)F^{(r)}(\tau)\,d\tau\right]. \quad (60)$$

From these equations it is clear that $F^{(t)}(t)$ and $F^{(r)}(t)$ denote respectively the normalized translational and angular velocity autocorrelation functions. The mixed autocorrelations are similarly extracted as

$$\left.\begin{aligned}\mathscr{L}[\langle\dot{\theta}(t)\dot{X}(0)\rangle]&=\langle\dot{X}(0)\dot{X}(0)\rangle\left[s^3(s+\gamma^{(t)})\Delta_2{}^{(r)}\,\Delta_2{}^{(t)}\frac{\Delta_1{}^{(r)}}{\Delta_1{}^{(t)}}\gamma^{(rt)}\right]\Big/\tilde{G}(s),\\ \mathscr{L}[\langle\dot{X}(t)\dot{\theta}(0)\rangle]&=\langle\dot{\theta}(0)\dot{\theta}(0)\rangle\left[s^3(s+\gamma^{(r)})\Delta_2{}^{(t)}\Delta_2{}^{(r)}\frac{\Delta_1{}^{(t)}}{\Delta_1{}^{(r)}}\gamma^{(tr)}\right]\Big/\tilde{G}(s),\end{aligned}\right\} \quad (61)$$

which vanish in the decoupled limit.

Alternatively, the sixteen autocorrelation functions listed in § 3 may be evaluated numerically as discussed below.

4.2. *Space rototranslation of the asymmetric top*

The multidimensional Markov equation (2) may be used to consider this general problem of single particle translation/rotation dynamics. In § 2 we have considered the simplest Mori approximant equivalent to order $n=1$. In general, however, for a finite, generic n, the relaxation process affecting the first memory kernel when the rotational part of the motion involves three Euler angles.

However, a general theory of asymmetric top space rototranslation may be developed using the Markovian set of equations (2). For example we consider the simple instance where the $(n+1)$th matrix is

$$\mathbf{A}_{n+1}=\begin{bmatrix}v_z\\ \\ \omega_z\end{bmatrix}.$$

A rotation–translation coupling exhibited by the friction (of dissipative) matrix γ (50) would be transmitted through the chain of ' virtual ' matrices $\mathbf{A}_1$ to $\mathbf{A}_n$ to the *real* $\mathbf{A}_{n+1}$. As a consequence we may take $\mathbf{A}_1$ to $\mathbf{A}_n$ as *diagonal*. This implies the following :

(i) The multidimensional Markov chain (2) removes the abstract memory kernel not only when dealing with the theory of single particle motion but also in the extensively developed field of hydrodynamics [6]. We may therefore relate conceptually the single and multi-particle theories within a Markovian framework for molecules of any symmetry moving in three dimensions. The extension of (50) to higher n may be interpreted physically for *planar* libration as equivalent to the addition of more ' cages ', or, in the constrained model, annuli, which naturally become larger in comparison with a molecular diameter. Eventually the outer cages are macroscopic entities whose movement is equivalent to co-operative rotation/translation of groups of molecules. The movement of the outer cages is conceptually similar to a vortex i.e. the translational part of the hydrodynamic spin density [19]. By analogy we may therefore use (2) to construct a generalized hydrodynamic formalism without assuming, for example, a frequency-dependent viscosity [20]. This would be equivalent to taking the Navier–Stokes equation and solving without firstly linearizing. It may therefore be possible to build up a theory of bulk phenomena from molecular considerations. One of the first tasks of such a theory would be to describe the vorticity phenomenon giving rise to the well-known extended negative tail of the velocity autocorrelation function as simulated by computer.

(ii) Our interpretation in terms of a mechanical model [21] such as the itinerant oscillator/librator eases the intuitive difficulty of understanding single molecule terms such as $\gamma^{(tr)}\gamma^{(rt)}$. By regarding (2) as a Markovian approximation to a physical reality involving multimolecular ensembles we may describe the action of the propeller in terms of a ' macroscopic ' model corresponding to a high-order Mori approximant. Development of the asymmetric top formalism allows us, of course, to consider also the motion of a *single molecule* shaped like a propeller, where there is no difficulty in imagining translation at time t in terms of rotation at $t=0$.

4.3. *Basis set*

Elsewhere [7, 9] we have constructed the Fokker–Planck equation describing the asymmetric top rototranslational itinerant oscillator with planar rotational constraints. To remove this for all n of (50) it is necessary to construct a basis set for the numerical solution of the diffusion equation expressed in matrix form.

denoted by

$$\mathbf{A}_n = (A_1^{(n)}, A_2^{(n)}, \ldots, A_m^{(n)}) \tag{62}$$

the basis set consists of the vectors

$$|H_m(\mathbf{A}_n) \exp(-\tfrac{1}{2}\|\mathbf{A}_n\|^2)\rangle, \tag{63}$$

where

$$H_m(\mathbf{A}_n) = H_{m_1}(A_1^{(n)}) H_{m_2}(A_2^{(n)} \ldots H_{m_n}(A_m^{(n)}). \tag{64}$$

Here H denotes the Hermite polynomial in standard notation. Consequently, the whole diffusion operator of the Fokker–Planck equation may be described by the basis set spanned by the direct products :

$$|H_{m_1}(\mathbf{A}_1) \exp(-\tfrac{1}{2}\|\mathbf{A}_1\| \ldots H_{m_n}(\mathbf{A}_n) \exp(-\tfrac{1}{2}\|\mathbf{A}_1\|^2)\rangle. \tag{65}$$

When inertial effects are negligible, our generalized Fokker–Planck equation, through integration over the velocity variables, should provide a diffusion equation identical with the one of Favro [17]. The most advantageous use of the multidimensional equation (2) will then be made using for the primary angular momentum variable the set of Wigner rotation matrices. In the most general case of space rototranslation this will be used in combination with the set represented by (65). Following the method outlined by Ferrario and Grigolini [7] one may then express the generalized Fokker–Planck equation in the form

$$\dot{\chi} = \mathbf{B}\chi, \tag{66}$$

where χ is a vector whose components are provided by the direct products of (65). Equation (66) may then be solved numerically, truncating the basis set in order to deal with a finite-dimensioned matrix. The end product of the computation will be spectra demonstrating the effects of asymmetry and finite rototranslational interaction on spectral observables such as the Legendre coefficients of orientation.

Finally, we note that by using as a primary variable the Wigner matrix corresponding to angular momentum we may avoid the intractable problem posed by the non-linearity of the rotational Euler–Langevin equations written in component form. The results of this generalization scheme will be published elsewhere.

Section 5

The comparison of analytical formulae for molecular rototranslation with experimental data and simulation results is a non-trivial task when there are present many phenomenological variables. We have attempted to produce formulae for a variety of situations amenable to true experimental observation. The analytical formulae may be individually tested by simulation. We suggest below some comparison procedures designed to evaluate separately each phenomenological variable.

5.1. *Langevin equations with rotational constraint*

In this case there are three variables λ_t, λ_r and $\lambda_{tr}{}^* \lambda_{rt}{}^*$. Dielectric and light scattering spectral data on polymer situations may be used in combination with data on all sixteen possible autocorrelation functions and associated time averages. It is known, of course, that the first Mori approximant is too crude in many respects. A far infrared measurement will demonstrate this very clearly since the theoretical return to transparency is far too slow, i.e. the characteristics of the Poley absorption are not reproduced except by recourse to a non-Markovian Mori equation.

5.2. *The constrained itinerant oscillator/librator*

In this case there are 7 parameters, $\Delta_1{}^{(t)^2}$, $\Delta_2{}^{(t)^2}$, $\Delta_1{}^{(r)^2}$, $\Delta_2{}^{(r)^2}$, $\gamma^{(t)}$, $\gamma^{(r)}$, and $\gamma^{(tr)}\gamma^{(rt)}$. However, it is known that $\Delta_2{}^{(t)^2}$ is the equilibrium mean square force and $\Delta_2{}^{(r)^2}$ the equilibrium mean square torque. $\Delta_1{}^{(t)^2}$ and $\Delta_2{}^{(t)^2}$ may similarly be defined in these terms. A suitable set of measurements may be the following. This is designed to measure the same specimen in seven different ways so that the parameters may be extracted in principle without recourse to least-mean-squares fitting. (In practice, of course, it is easier to iterate on the results of each experiment to establish whether the results are self consistent.)

(1) Far infrared/dielectric spectroscopy ; the first Legendre (orientational) correlation function, related to $\langle\omega(t)\omega(0)\rangle$ by macro–micro correlation.
(2) Depolarized Rayleigh scattering ; the second Legendre function.
(3) Incoherent, inelastic neutron scattering ; further Legendre functions.
(4) Spin–spin N.M.R. relaxation ; second Legendre correlation time.
(5) Spin–rotation N.M.R. relaxation angular momentum correlation time.
(6) van't Hove self correlation function ; the bivariate p.d.f.
(7) Tracer diffusion measurements, linear velocity correlation time.

In addition to this set of seven experiments the same specimen may be simulated by molecular dynamics. The analytical theory is required to reproduce *all* the available data self-consistently and there is, in effect, no redundancy (or over-flexibility) involved in the proper use of the seven parameters. On the contrary, this model is still a very early approximant of an infinite continued fraction of matrices whose convergence has scarcely been tested experimentally. It would therefore be remarkable if seven parameters were enough to describe the variety of available data satisfactorily even at only one thermodynamic state.

5.3. *Three-dimensional itinerant oscillation/libration of the asymmetric top*

In this case the friction coefficients $\boldsymbol{\gamma}^{(r)}$, $\boldsymbol{\gamma}^{(tr)}$ and $\boldsymbol{\gamma}^{(rt)}$ are diagonal matrices so that the theory involves parameters such as $\gamma_{xx}{}^{(r)}$, $\gamma_{yy}{}^{(r)}$, $\gamma_{zz}{}^{(r)}$, and the matrix product coefficients $\gamma_{xx}{}^{(tr)}\gamma_{xx}{}^{(rt)}$, $\gamma_{yy}{}^{(tr)}\gamma_{yy}{}^{(rt)}$, and $\gamma_{zz}{}^{(tr)}\gamma_{zz}{}^{(rt)}$. However, the asymmetry provides us with an opportunity to simulate more equilibrium averages.

6. Discussion

In this article we have attempted to set out a theory of single particle rototranslation and to indicate how this may be evaluated with a suitably wide range of data. A direct comparison with the simulator is possible without making

with. There is sometimes considerable doubt when dealing with ... field problem of dielectric spectroscopy, collision induced absorption in absorption and scattering spectroscopy, etc. Although some experimental relaxation methods deal with single particle information (N.M.R., incoherent, inelastic neutron scattering), macro–micro correlation theorems are required ideally to relate the many particle information of far infrared/dielectric relaxation and light scattering to the single-particle theory developed here. These theorems are obtainable with the use of Mori theory keeping the resonance matrix $\boldsymbol{\Omega}_{\mathbf{A}}$ finite. Their development for rototranslation will be the subject of future work.

The S.R.C. is thanked for extensive financial support.

Appendix

Here we explain why the off-diagonal elements of the friction (or dissipative) matrix survive the symmetry theorems of time reversal, parity and reflection.

Time reversal symmetry

Consider the column vector of linear and angular momentum

$$\mathbf{A} = \begin{bmatrix} \mathbf{p} \\ \\ \mathbf{J} \end{bmatrix} \tag{A 1}$$

for the space reorientation of the asymmetric top. The vectors $\mathbf{p}$ and $\mathbf{J}$ have the same time reversal symmetry (since $\mathbf{J}$ may always be written at the same instant in time as $\mathbf{R} \times \mathbf{p}$ where $\mathbf{R}$ is a position vector invariant under time reversal). It follows that the resonance frequency matrix $\boldsymbol{\Omega}_{\mathbf{A}}$ is null provided the total hamiltonian is invariant to time reversal (i.e. if there is no applied unidirectional external field). The mixed autocorrelation function $\langle \mathbf{p}(0) \, . \, \mathbf{J}(0) \rangle$ vanishes but $\langle \mathbf{p}(0) \, . \, \mathbf{J}(t) \rangle$ does *not* do so on the grounds of time-reversal symmetry.

Parity

This transformation inverts all atomic positions and molecular momentum, and $\langle \mathbf{p}(0) \, . \, \mathbf{J}(t) \rangle$ would vanish for all t if $\mathbf{p}$ and $\mathbf{J}$ were to have different parity provided the total hamiltonian is parity invariant and the molecules have a centre of symmetry. We are dealing in some cases in this paper with the rototranslation of the asymmetric top whose rotational motion is constrained about the laboratory z axis, but whose centre of mass translation is through three-dimensional space. $\mathbf{J}(t)$ therefore reduces to $I\omega_z \mathbf{k}$. In general the asymmetric top has no centre of symmetry and in general there is no analytical relation between $\mathbf{v}(0)$ and $\omega_z(t)$.

It is not possible to relate the parity of $\mathbf{J}(t)$ to that of $\mathbf{v}(0)$ or *vice-versa* and there is consequently no reason why the mixed autocorrelation functions should not exist for $t > 0$.

Reflection symmetry

In a system with reflection symmetry properties which transform differently under reflection are uncorrelated for all time. This transform reflects all linear of the coordinate system because they are not scalars, and again there is no reason why the mixed autocorrelation functions, and therefore the off diagonal elements of the dissipative matrix, should not exist, even for symmetries such as that of N_2, or the spherical top with an embedded reference vector such as a dipole moment.

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