Langevin equation method for the rotational Brownian motion and orientational relaxation in liquids: II. Symmetrical top molecules

Langevin equation method for the rotational Brownian motion and orientational relaxation in liquids: II. Symmetrical top molecules

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Abstract
A theory of orientational relaxation for the inertial rotational Brownian motion of a symmetric top molecule is developed using the Langevin equation rather than the Fokker–Planck equation. The infinite hierarchy of differential-recurrence relations for the orientational correlation functions for the relaxation behaviour is derived by averaging the corresponding Euler–Langevin equations. The solution of this hierarchy is obtained using matrix continued fractions allowing the calculation of the correlation times and the spectra of the orientational correlation functions for typical values of the model parameters.

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(Some figures in this article are in colour only in the electronic version)

1. Introduction

Models of the inertial rotational Brownian motion are frequently used in studying orientational relaxation in liquids in order to compare spectra obtained by various probe techniques such as dielectric relaxation, the dynamic Kerr effect, infrared absorption, Raman scattering, etc with the corresponding theoretical spectra [1–3]. Hitherto the theoretical treatment of rotational Brownian motion has been mainly based on the corresponding Fokker–Planck equation [4]. This equation is a partial differential equation for the time evolution of the orientational distribution function of a molecule in phase space. It is derived by calculating the drift and the diffusion coefficients from the inertial Euler–Langevin equation which governs the time behaviour of the set of random variables describing the rotational Brownian motion of a molecule in a fluid. The solution of the Fokker–Planck equation has been usually obtained by

separating the variables. A comprehensive discussion of the Fokker–Planck equation method and its applications to orientational relaxation in fluids is given, e.g., in [1, 3, 5–14].

An alternative approach to the problem has been given by Coffey [15, 16] and Coffey *et al* [17–19]. They developed a method of solution of the Langevin equations for simple models of the inertial rotation of linear rotators without recourse to the Fokker–Planck equation. The key step in applying the method is first to convert by appropriate transformation the Langevin equation into an equation for the quantity the statistical average of which is desired. That equation is then averaged over its realizations in phase space. The transformed Langevin equation contains not only the quantity the average of which is desired but also the next higher order average and so on. It is thus the generating equation of a hierarchy of averages which can be solved by a variety of methods. This procedure entirely eliminates the excessive step in the theory of constructing and solving the corresponding Fokker–Planck equation. The advantage in computational labour that the averaging method has over the Fokker–Planck solution is considerable, neither the derivation of that equation nor knowledge of the intricate transformations used to effect separation of the variables in it, and to solve the resulting simultaneous recurrence relations is required. The advantages of the Langevin equation method have been amply demonstrated in a recent paper [20]. There a theory of orientational relaxation for the inertial rotational Brownian motion of a *linear molecule* (rotator in space) has been developed, the infinite hierarchy of differential-recurrence relations for the orientational correlation functions describing the relaxation behaviour of the system has been derived and the solution of this hierarchy has been obtained in terms of continued fractions. Here, the Langevin equation approach for rigid rotators proposed in [20] is generalized to the orientational relaxation of an assembly of *symmetrical top* molecules undergoing rotational Brownian motion in space.

2. Rotational Brownian motion of a symmetrical top molecule

We consider the rotational Brownian motion of a symmetric top molecule. In the molecular coordinate system $oxyz$ rigidly connected to the top, the angular velocity $\boldsymbol{\omega}$ and the angular momentum $\mathbf{M}$ are defined as [1]

$$\boldsymbol{\omega} = (\omega_x, \omega_y, \omega_z) = (\dot{\vartheta}, \dot{\varphi} \sin \vartheta, \dot{\psi} + \dot{\varphi} \cos \vartheta) \tag{1}$$

and

$$\mathbf{M} = (I\omega_x, I\omega_y, I_z\omega_z) \tag{2}$$

where I and I_z are the components of the moment of inertia tensor, ϑ, φ and ψ are the Euler angles (ϑ is the angle between the axes of symmetry of the molecule and the Z axes of the laboratory coordinate system, φ is the azimuthal angle and ψ is the angle characterizing rotation about the axis of symmetry). In the absence of external fields, the rotational Brownian motion of the top is governed by the vector Euler–Langevin equation [1, 18]

$$\frac{\mathrm{d}}{\mathrm{d}t}\mathbf{M}(t) + \boldsymbol{\omega}(t) \times \mathbf{M}(t) + \zeta \boldsymbol{\omega}(t) = \boldsymbol{\lambda}(t) \tag{3}$$

where $\zeta \boldsymbol{\omega}(t)$ and $\boldsymbol{\lambda}(t)$ are the frictional and white noise torques arising from the Brownian motion of the surroundings, respectively. The white noise torque has the following properties:

$$\overline{\lambda_j(t)} = 0 \qquad \overline{\lambda_j(t)\lambda_m(t')} = 2k_B T \zeta \delta_{j,m} \delta(t - t') \qquad (j, m = x, y, z) \tag{4}$$

where k_B is the Boltzmann constant, T is the temperature, ζ is the friction (drag) tensor, $\delta(t)$ is the Dirac-delta function, $\delta_{j,m}$ is Kronecker's delta and the overbar means the statistical average over an ensemble of rotators that all start at the instant t with the same sharp values of the

angular velocity and the orientation. The $\lambda_j(t)$ must also satisfy Isserlis's theorem [19] for centred Gaussian random variables, namely for $2n$ λ's

$$\overline{\lambda_j(t_1)\lambda_j(t_2)\cdots\lambda_j(t_{2n})} = \overline{\lambda_1\lambda_2\cdots\lambda_{2n}} = \sum \prod_{k_p < k_s} \overline{\lambda_{k_p}\lambda_{k_s}} \tag{5}$$

where the sum is taken over all distinct products of expectation value pairs, each of which is formed by selecting n pairs of time intervals from $2n$ time points and for $2n + 1$ λ's

$$\overline{\lambda_j(t_1)\lambda_j(t_2)\cdots\lambda_j(t_{2n+1})} = 0. \tag{6}$$

We proceed by noting that equation (3) rewritten for the vector components in the molecular frame becomes

$$I\dot{\omega}_x(t) = -\omega_y(t)(I_z\omega_z(t) - I\omega_y(t)\cot\vartheta) - \zeta\omega_x(t) + \lambda_x(t) \tag{7}$$

$$I\dot{\omega}_y(t) = \omega_x(t)(I_z\omega_z(t) - I\omega_y(t)\cot\vartheta) - \zeta\omega_y(t) + \lambda_y(t) \tag{8}$$

$$I_z\dot{\omega}_z(t) = -\zeta_z\omega_z(t) + \lambda_z(t). \tag{9}$$

Equations (7)–(9) combined with

$$\dot{\vartheta}(t) = \omega_x(t) \qquad \dot{\varphi}(t) = \omega_y(t)/\sin\vartheta(t) \qquad \dot{\psi}(t) = \omega_z(t) - \omega_y(t)\cot\vartheta(t) \tag{10}$$

(which follow from the definition of the angular velocity components equation (1)) constitute a system of non-linear stochastic differential equations. In order to proceed, we shall use the Stratonovich definition [21] of the average of equations (7)–(9). Thus, it is unnecessary to transform the Langevin equations (7)–(9) to Itô equations; moreover, one can apply the usual rules of calculus (e.g., [22]).

As far as the majority of applications is concerned, the quantities of interest are the orientational equilibrium correlation functions (CFs) $C_l(t)$ for the Legendre polynomials $P_l[\cos\vartheta(t)]$ defined as

$$C_l(t) = \langle P_l[\cos\vartheta(0)]P_l[\cos\vartheta(t)]\rangle \tag{11}$$

(the angular brackets denote the *equilibrium* ensemble averages). These averages characterize the orientational relaxation in liquids. Having determined the correlation function $C_l(t)$, one can also evaluate the corresponding orientational correlation time τ_l defined as the area under the normalized correlation function $C_l(t)/C_l(0)$ [3], namely

$$\tau_l = \frac{1}{C_l(0)} \int_0^\infty C_l(t)\,\mathrm{d}t. \tag{12}$$

We shall show below how the first- and the second-order equilibrium orientational CFs (namely $C_1(t)$ and $C_2(t)$) can be calculated in the context of the Langevin equation approach (these CFs are used for the interpretation of dielectric and infrared absorption and Raman and Rayleigh scattering measurements) [2].

In order to calculate the $C_l(t)$, we introduce the functions

$$f_{n,k}^{l,m}(t) = P_l^{|m|}[\cos\vartheta(t)]s_{n,k}^m[\omega_x(t), \omega_y(t), \omega_z(t)] \tag{13}$$

where $P_l^{|m|}(z)$ are the associated Legendre functions [23] and the functions $s_{n,k}^m(\omega_x, \omega_y, \omega_z)$ $(l, n, k = 0, 1, 2, \ldots; -l \leqslant m \leqslant l)$ are expressed as finite series of products of Hermite polynomials $H_n(z)$ [23] in the components ω_x, ω_y and ω_z of the angular velocity, namely

$$s_{n,k}^{2m-M}(\omega_x, \omega_y, \omega_z) = H_k(\eta_z\omega_z)\sum_{q=0}^n \frac{r_{2m-M}(n,q)}{q!(n-q)!} H_{2n-2q+M-\varepsilon_m}(\eta\omega_x)H_{2q+\varepsilon_m}(\eta\omega_y). \tag{14}$$

Here $\eta = \sqrt{I/(2k_BT)}$, $\eta_z = \sqrt{I_z/(2k_BT)}$, $\varepsilon_m = 0$ for $m \geqslant 0$, $\varepsilon_m = 1$ for $m < 0$, $M = 0$ or 1 and the coefficients $r_{2m+M}(n, q)$ of the finite series are determined by the recurrence relations

$$r_{2m}(n, q) = \left(n - q + \frac{1}{2}\right)\left(1 - \frac{2q+1}{2m-1}\right)r_{2m-1}(n, q) + (n - q)\frac{(2q+1)}{2m-1}r_{2m-1}(n, q + 1)$$

(15)

$$r_{2m+1}(n, q) = \left(1 + \frac{q}{m}\right)r_{2m}(n, q) - \frac{q}{m}r_{2m}(n, q - 1)$$ (16)

$$r_{-2m}(n, q) = (n - q)\left[\left(1 - \frac{2q+2}{2m-1}\right)r_{-(2m-1)}(n, q) + \frac{2q+3}{2m-1}r_{-(2m-1)}(n, q + 1)\right]$$ (17)

$$r_{-(2m+1)}(n, q) = \left(1 + \frac{2q+1}{2m}\right)r_{-2m}(n, q) - \frac{q}{2m}\left(2 - \frac{1}{n-q+1}\right)r_{-2m}(n, q - 1)$$ (18)

with $r_0(n, q) = r_{\pm 1}(n, q) = 1$ and $m \geqslant 0$. The above recurrence relations and the orthogonality of the Hermite polynomials guaranty that the functions $s_{n,k}^m(\omega_x, \omega_y, \omega_z)$ are orthogonal, namely

$$\int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} s_{n,k}^m(\omega_x, \omega_y, \omega_z)s_{n',k'}^{m'}(\omega_x, \omega_y, \omega_z)\,\mathrm{e}^{-\eta^2(\omega_x^2+\omega_y^2)-\eta_z^2\omega_z^2}\,\mathrm{d}\omega_x\,\mathrm{d}\omega_y\,\mathrm{d}\omega_z \sim \delta_{n,n'}\delta_{m,m'}\delta_{k,k'}$$

and that they form a complete set in angular velocity space. It is obvious from the definition of equation (13) that $f_{0,0}^{l,0}(t) = P_l[\cos\vartheta(t)]$. We remark that in the present paper, we are interested in orientational CFs (11), which are independent of the azimuthal angle φ, therefore, this angle does not appear in equation (13); in the general case, one can take into account the dependence on the angle φ by introducing the factor $\mathrm{e}^{\mathrm{i}m\varphi}$ in equation (13).

We desire equations for the averaged values of $\overline{f_{n,k}^{l,m}(t)}$ over its realizations in phase space (here configuration—angular velocity space). This is accomplished by evaluating (following the appropriate transformation of the variables in equations (7)–(9) and subsequent use of Isserlis's theorem)

$$\frac{\mathrm{d}}{\mathrm{d}t}\overline{f_{n,k}^{l,m}(t)}$$

$$= \lim_{\tau \to 0}\frac{\overline{P_l^{|m|}[\cos\vartheta(t+\tau)]s_{n,k}^m[\omega_x(t+\tau), \omega_y(t+\tau), \omega_z(t+\tau)] - P_l^{|m|}(\cos\vartheta)s_{n,k}^m(\omega_x, \omega_y, \omega_z)}}{\tau}$$

(19)

where

$$\omega_x(t+\tau) = \omega_x - \frac{\zeta}{I}\int_t^{t+\tau}\omega_x(t')\,\mathrm{d}t'$$
$$- \int_t^{t+\tau}\omega_y(t')\left[\frac{I_z}{I}\omega_z(t') - \omega_y(t')\cot\vartheta(t')\right]\mathrm{d}t' + \frac{1}{I}\int_t^{t+\tau}\lambda_x(t')\,\mathrm{d}t'$$ (20)

$$\omega_y(t+\tau) = \omega_y - \frac{\zeta}{I}\int_t^{t+\tau}\omega_y(t')\,\mathrm{d}t'$$
$$+ \int_t^{t+\tau}\omega_x(t')\left[\frac{I_z}{I}\omega_z(t') - \omega_y(t')\cot\vartheta(t')\right]\mathrm{d}t' + \frac{1}{I}\int_t^{t+\tau}\lambda_y(t')\,\mathrm{d}t'$$ (21)

$$\omega_z(t+\tau) = \omega_z - \frac{\zeta}{I_z}\int_t^{t+\tau}\omega_z(t')\,\mathrm{d}t' + \frac{1}{I_z}\int_t^{t+\tau}\lambda_z(t')\,\mathrm{d}t'$$ (22)

are integral forms of equations (7)–(9). We remark that the time τ is assumed to be of such short duration that the angular velocities do not significantly alter during τ neither does any

external conservative torque. Nevertheless τ is supposed sufficiently long that the chance that the rapidly fluctuating stochastic torque $\lambda(t)$ takes on a given value at time $t + \tau$ is independent of the value which the torque possessed at time t. We further remark that ϑ, ω_x, ω_y and ω_z and $\vartheta(t)$, $\omega_x(t)$, $\omega_y(t)$ and $\omega_z(t)$ in equation (19) have different meanings, namely, $\vartheta(t)$, $\omega_x(t)$, $\omega_y(t)$ and $\omega_z(t)$ are stochastic variables (processes) while ϑ, ω_x, ω_y and ω_z are the sharp values at time t (recall that the time τ is infinitesimally small). Instead of using different symbols for the two quantities, we have distinguished the sharp values at time t from the stochastic variables by deleting the time argument as in [19].

Thus by evaluating the right-hand side of equation (19) explicitly, we can derive the differential-recurrence relations (recurring in the three numbers, namely m, n, k) for the moments $\overline{f_{n,k}^{l,m}}$ (the derivation is given in appendix A):

$$\eta \frac{d}{dt} \overline{f_{n,k}^{l,0}} = -[2n\beta' + k\beta_z'/B]\overline{f_{n,k}^{l,0}} + \frac{1}{2}\overline{f_{n,k}^{l,1}} + 2\overline{f_{n-1,k}^{l,1}} \tag{23}$$

$$\begin{aligned}
\eta \frac{d}{dt} \overline{f_{n,k}^{l,\pm(2m-M)}} &= -[(2n+M)\beta' + k\beta_z'/B]\overline{f_{n,k}^{l,\pm(2m-M)}} + \overline{f_{n-1+M,k}^{l,\pm(2m+1-M)}} \\
&\quad + \frac{1}{4}\overline{f_{n+M,k}^{l,\pm(2m+1-M)}} - (1 - \delta_{\pm(2m-M),-1})(l + 2m - M)(l - 2m + 1 + M) \\
&\quad \times \left[(n+m)\overline{f_{n-1+M,k}^{l,\pm(2m-1-M)}} + \frac{(n-m+1+M)}{4}\overline{f_{n+M,k}^{l,\pm(2m-1-M)}} \right] \\
&\quad \mp (2m-M)\sqrt{B}\left(\frac{1}{2}\overline{f_{n,k+1}^{l,\mp(2m-M)}} + k\overline{f_{n,k-1}^{l,\mp(2m-M)}} \right).
\end{aligned} \tag{24}$$

Here $m > 0$, $\beta' = \eta\zeta/I$, $\beta_z' = \eta\zeta_z/I$ and $B = I_z/I$. For linear molecules ($I_z = 0$, $\beta_z' = 0$), equations (23) and (24) yield the results of [20]. All the quantities $\overline{f_{n,k}^{l,m}}$ in the three number recurrence relations (23) and (24) are functions of the *sharp* values ϑ, ω_x, ω_y and ω_z, which are themselves random variables with the probability density function $W(\vartheta, \omega_x, \omega_y, \omega_z, t)$. Therefore, in order to obtain equations for the moments governing the relaxation dynamics of the system, we must also average equations (23) and (24) over W [19]. However, if a system is in equilibrium as in the present problem all such averages are either constant or zero indicating that one must first construct from equations (23) and (24) a set of differential-recurrence equations for the appropriate equilibrium CFs [19, 20].

3. Evaluation of $\tilde{C}_1$

Following [20], one may also readily derive differential-recurrence equations for the equilibrium CF for the first Legendre polynomial ($l = 1$), namely $c_{n,k}^{1,m}(t) = \left\langle \cos\vartheta(0) \overline{f_{n,k}^{1,m}(t)} \right\rangle$ (so that $c_{0,0}^{1,0}(t) \equiv C_1(t)$) by multiplying equations (23) and (24) by $\cos\vartheta(0)$ and by averaging the equations so obtained over the equilibrium distribution function W_0 at the instant $t = 0$. These equations can be written as a system of algebraic recurrence relations in the frequency domain using Laplace transformation, namely

$$[\eta s + 2n\beta' + k\beta_z'/B]\tilde{c}_{n,k}^{1,0} = \eta c_{0,0}^{1,0}(0)\delta_{n+k,0} + \frac{1}{2}\tilde{c}_{n,k}^{1,1} + 2\tilde{c}_{n-1,k}^{1,1} \tag{25}$$

$$[\eta s + (2n+1)\beta' + k\beta_z'/B]\tilde{c}_{n,k}^{1,1} = -\frac{1}{2}(n+1)\tilde{c}_{n+1,k}^{1,0} - 2(n+1)\tilde{c}_{n,k}^{1,0} - \frac{1}{2}\sqrt{B}\left(\tilde{c}_{n,k+1}^{1,-1} + 2k\tilde{c}_{n,k-1}^{1,-1}\right) \tag{26}$$

$$[\eta s + (2n+1)\beta' + k\beta_z'/B]\tilde{c}_{n,k}^{1,-1} = \frac{1}{2}\sqrt{B}\left(\tilde{c}_{n,k+1}^{1,1} + 2k\tilde{c}_{n,k-1}^{1,1}\right) \tag{27}$$

where $\tilde{c}(s) = L\{c(t)\} = \int_0^\infty e^{-st} c(t)\, dt$. Here, we note that all the $c_{n,k}^{1,0}(0)$ vanish with the exception of $n + k = 0$, namely $c_{0,0}^{1,0}(0) = 1/3$ (this result follows from the orthogonality property of the associated Legendre functions [25]). Equations (25)–(27) can be reduced to equations (3.18a)–(3.18d) of Morita [12] (obtained via the Fokker–Planck equation) by introducing new functions $A_{n,k}$, $B_{n,k}$ and $C_{n,k}$ (in Morita's notation), namely

$$A_{n,k} = \frac{(-1)^{n+k}}{n!2^{4n}(2k)!!\eta^{2n}\eta_z^k} \tilde{c}_{n,k}^{1,0} \qquad \left\{ \begin{matrix} B_{n,k} \\ C_{n,k} \end{matrix} \right\} = \frac{(-1)^{n+k}}{(n+1)!2^{4n+2}(2k)!!\eta^{2n+1}\eta_z^k} \left\{ \begin{matrix} \tilde{c}_{n,k}^{1,1} \\ \tilde{c}_{n,k}^{1,-1} \end{matrix} \right\}.$$

In order to solve the hierarchy of recurrence equations (25)–(27), we introduce a supercolumn vector $\mathbf{C}_n(t)$ comprising three subvectors:

$$\mathbf{C}_n(t) = \begin{pmatrix} \mathbf{c}_{n-1}^{1,0}(t) \\ \mathbf{c}_{n-1}^{1,1}(t) \\ \mathbf{c}_{n-1}^{1,-1}(t) \end{pmatrix} \qquad \mathbf{c}_n^{1,m}(t) = \begin{pmatrix} c_{n,0}^{1,m}(t) \\ c_{n-1,1}^{1,m}(t) \\ \vdots \\ c_{0,n}^{1,m}(t) \end{pmatrix}. \tag{28}$$

The subvector $\mathbf{c}_n^{1,m}(t)$ has dimension $n+1$. The three index recurrence equations (25)–(27) for $c_{n,k}^{1,m}(t)$ can then be transformed into the matrix three-term differential-recurrence equation

$$\eta \frac{d}{dt} \mathbf{C}_n(t) = \mathbf{Q}_n^- \mathbf{C}_{n-1}(t) + \mathbf{Q}_n \mathbf{C}_n(t) + \mathbf{Q}_n^+ \mathbf{C}_{n+1}(t) \qquad (n \geqslant 1) \tag{29}$$

where $\mathbf{C}_0(t) = \mathbf{0}$,

$$\mathbf{Q}_n^- = \begin{pmatrix} \mathbf{0} & \mathbf{q}_n^- & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & -\mathbf{p}_n^- \\ \mathbf{0} & \mathbf{p}_n^- & \mathbf{0} \end{pmatrix}$$

$$\mathbf{Q}_n^+ = \begin{pmatrix} \mathbf{0} & \mathbf{0} & \mathbf{0} \\ \mathbf{q}_n^+ & \mathbf{0} & -\mathbf{p}_n^+ \\ \mathbf{0} & \mathbf{p}_n^+ & \mathbf{0} \end{pmatrix}$$

$$\mathbf{Q}_n = \begin{pmatrix} \mathbf{q}_n^0 & \mathbf{I}_n/2 & \mathbf{0} \\ 2(\mathbf{r}_n - \mathbf{I}_n) & \mathbf{q}_n^1 & \mathbf{0} \\ \mathbf{0} & \mathbf{0} & \mathbf{q}_n^1 \end{pmatrix}$$

and

$$\mathbf{q}_n^- = 2 \begin{pmatrix} 1 & 0 & \cdots & 0 \\ 0 & 1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 1 \\ 0 & 0 & \cdots & 0 \end{pmatrix}_{n \times (n-1)} \tag{30}$$

$$\mathbf{q}_n^+ = -\frac{1}{2} \begin{pmatrix} n & 0 & \cdots & 0 & 0 \\ 0 & n-1 & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & 0 \end{pmatrix}_{n \times (n+1)} \tag{31}$$

$$\mathbf{p}_n^- = \sqrt{B} \begin{pmatrix} 0 & \cdots & 0 & 0 \\ 1 & \cdots & 0 & 0 \\ \vdots & \ddots & \vdots & \vdots \\ 0 & \cdots & n-2 & 0 \\ 0 & \cdots & 0 & n-1 \end{pmatrix}_{n \times (n-1)} \tag{32}$$

$$\mathbf{p}_n^+ = \frac{\sqrt{B}}{2} \begin{pmatrix} 0 & 1 & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & 0 \\ 0 & 0 & \cdots & 0 & 1 \end{pmatrix}_{n \times (n+1)} \tag{33}$$

$$\mathbf{r}_n = - \begin{pmatrix} n-1 & 0 & \cdots & 0 \\ 0 & n-2 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 0 \end{pmatrix}_{n \times n} \tag{34}$$

$$\mathbf{q}_n^M = \begin{pmatrix} f^M(n-1,0) & 0 & \cdots & 0 \\ 0 & f^M(n-2,1) & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & f^M(0,n-1) \end{pmatrix}_{n \times n}. \tag{35}$$

Here $f^M(n,k) = -(2n+M)\beta' - k\beta'_z/B$ and $\mathbf{I}_n$ is the unit matrix which has dimension $n \times n$.

The initial conditions are

$$\mathbf{C}_1(0) = \begin{pmatrix} 1/3 \\ 0 \\ 0 \end{pmatrix} \qquad \text{and} \qquad \mathbf{C}_n(0) = \mathbf{0} \qquad \text{for all} \quad n \geqslant 2.$$

On taking the Laplace transform of equation (29), we have the matrix three-term recurrence relation

$$(\eta s \mathbf{I}_{3n} - \mathbf{Q}_n)\tilde{\mathbf{C}}_n(s) - \mathbf{Q}_n^+ \tilde{\mathbf{C}}_{n+1}(s) - \mathbf{Q}_n^- \tilde{\mathbf{C}}_{n-1}(s) = \delta_{n,1} \eta \mathbf{C}_1(0) \qquad (n \geqslant 1). \tag{36}$$

The exact solution, for the Laplace transform $\tilde{\mathbf{C}}_1(s)$, is then given by the matrix continued fraction [19]

$$\tilde{\mathbf{C}}_1(s) = \eta \cfrac{\mathbf{I}_3}{\eta s \mathbf{I}_3 - \mathbf{Q}_1 - \mathbf{Q}_1^+ \cfrac{\mathbf{I}_6}{\eta s \mathbf{I}_6 - \mathbf{Q}_2 - \mathbf{Q}_2^+ \cfrac{\mathbf{I}_9}{\eta s \mathbf{I}_9 - \mathbf{Q}_3 \,\cdots} \mathbf{Q}_3^-} \mathbf{Q}_2^-} \mathbf{C}_1(0) \tag{37}$$

where the fraction lines denote matrix inversion. Having determined the spectrum $\tilde{C}_1(i\omega) = \tilde{c}_{0,0}^{1,0}(i\omega)$ from equation (37), one can also evaluate the orientational correlation time $\tau_1 = \tilde{C}_1(0)/C_1(0)$ (equation (12) for $n = 1$) and the normalized complex susceptibility $\hat{\chi}(\omega) = \hat{\chi}'(\omega) - i\hat{\chi}''(\omega)$. This is given by linear response theory as [21]

$$\hat{\chi}(\omega) = \frac{\chi(\omega)}{\chi'(0)} = 1 - i\omega \frac{\tilde{c}_{0,0}^{1,0}(i\omega)}{c_{0,0}^{1,0}(0)} \tag{38}$$

where $\chi'(0) = N\mu^2/3k_B T$ is the static susceptibility, N is the number of dipoles per unit volume and μ is the dipole moment of a molecule.

For linear ($I_z = 0$) and spherical top ($I = I_z$) molecules, the results of numerical calculations based on equation (37) for linear ($I_z = 0$) and spherical top ($I = I_z$) molecules were compared with those of Sack [6] (Sack obtained the solutions in terms of ordinary continued fractions). For linear molecules this is equation (27) of [20] and for spherical tops Sack's continued fraction solution [6] is (in our notation)

$$\tilde{C}_1(s) = \cfrac{\eta/3}{s\eta + \cfrac{1}{s\eta + \beta' + \cfrac{1}{2(s\eta + 2\beta')} + \cfrac{(3-1/2)/2}{s\eta + 2\beta' + \cfrac{2}{s\eta + 3\beta' + \cfrac{1}{3(s\eta + 4\beta')} + \cfrac{(5-1/3)/2}{s\eta + 4\beta' + \cdots}}}}}$$

(39)

(equation (39) is derived in appendix B). The numerical calculation indicates that the matrix equation (37) and ordinary continued fraction solutions, equation (27) of [20] and equation (39), yield the same results.

4. Evaluation of $\tilde{C}_l$ for an arbitrary l

In like manner we can derive differential-recurrence equations for the equilibrium CF $c_{n,k}^{l,m}(t) = \langle P_l[\cos\vartheta(0)]\overline{f_{n,k}^{l,m}(t)}\rangle$ so that $c_{0,0}^{l,0}(t) \equiv C_l(t)$. This is accomplished by multiplying equations (23) and (24) by $P_l[\cos\vartheta(0)]$ and averaging the equations so obtained over the equilibrium distribution function W_0 at the instant $t = 0$. In order to evaluate the lth-order equilibrium orientation correlation function $C_l(t)$, the $2l + 1$ independent equations (23) and (24) must be considered. Hence, the solution can be given in terms of matrix continued fractions. In order to solve the hierarchy of moment equations so obtained, we introduce the supercolumn vector $\mathbf{C}_n(t)$ comprising $2l + 1$ subvectors

$$\mathbf{C}_n(t) = \begin{pmatrix} \mathbf{c}_{n-1}^{l,0}(t) \\ \mathbf{c}_{n-1}^{l,1}(t) \\ \mathbf{c}_{n-1}^{l,-1}(t) \\ \vdots \\ \mathbf{c}_{n-1}^{l,l}(t) \end{pmatrix} \qquad \mathbf{c}_n^{l,m}(t) = \begin{pmatrix} c_{n,0}^{l,m}(t) \\ c_{n-1,1}^{l,m}(t) \\ \vdots \\ c_{0,n}^{l,m}(t) \end{pmatrix}.$$

(40)

Then the hierarchy of equations can be transformed into the matrix three-term differential-recurrence equation (29), where $\mathbf{Q}_n$, $\mathbf{Q}_n^+$ and $\mathbf{Q}_n^-$ are matrices with elements to be determined from equations (23) and (24). The initial conditions are given by the supercolumn vector

$$\mathbf{C}_1(0) = \begin{pmatrix} 1/(2l+1) \\ 0 \\ \vdots \\ 0 \end{pmatrix} \qquad \text{and} \qquad \mathbf{C}_n(0) = \mathbf{0} \qquad \text{for all} \quad n \geqslant 2.$$

The exact solution for the Laplace transform $\tilde{\mathbf{C}}_1(s)$ is similar to that given by equation (37). An explicit solution for $l = 2$ is now presented as an example.

By multiplying equations (23) and (24) by $P_2[\cos\vartheta(0)]$ and by averaging the equations so obtained over the equilibrium distribution function W_0 at the instant $t = 0$, we have for $l = 2$

$$[\eta s + 2n\beta' + k\beta_z'/B]\tilde{c}_{n,k}^{2,0} = \eta c_{0,0}^{2,0}(0)\delta_{n+k,0} + \tfrac{1}{2}\tilde{c}_{n,k}^{2,1} + 2\tilde{c}_{n-1,k}^{2,1}$$

(41)

$$[\eta s + (2n+1)\beta' + k\beta_z'/B]\tilde{c}_{n,k}^{2,1} = -\tfrac{3}{2}(n+1)\tilde{c}_{n+1,k}^{2,0} - 6(n+1)\tilde{c}_{n,k}^{2,0}$$
$$+ \tfrac{1}{4}\tilde{c}_{n+1,k}^{2,2} + \tilde{c}_{n,k}^{2,2} - \tfrac{1}{2}\sqrt{B}\left(\tilde{c}_{n,k+1}^{2,-1} + 2k\tilde{c}_{n,k-1}^{2,-1}\right)$$

(42)

$$[\eta s + (2n+1)\beta' + k\beta'_z/B]\tilde{c}^{2,-1}_{n,k} = \tfrac{1}{4}\tilde{c}^{2,-2}_{n+1,k} + \tilde{c}^{2,-2}_{n,k} + \tfrac{1}{2}\sqrt{B}\big(\tilde{c}^{2,1}_{n,k+1} + 2k\tilde{c}^{2,1}_{n,k-1}\big) \tag{43}$$

$$[\eta s + 2n\beta' + k\beta'_z/B]\tilde{c}^{2,2}_{n,k} = -n\tilde{c}^{2,1}_{n,k} - 4(n+1)\tilde{c}^{2,1}_{n-1,k} - \sqrt{B}\big(\tilde{c}^{2,-2}_{n,k+1} + 2k\tilde{c}^{2,-2}_{n,k-1}\big) \tag{44}$$

$$[\eta s + 2n\beta' + k\beta'_z/B]\tilde{c}^{2,-2}_{n,k} = -n\tilde{c}^{2,-1}_{n,k} - 4(n+1)\tilde{c}^{2,-1}_{n-1,k} + \sqrt{B}\big(\tilde{c}^{2,2}_{n,k+1} + 2k\tilde{c}^{2,2}_{n,k-1}\big) \tag{45}$$

where $c^{2,m}_{n,k}(t) = \big\langle P_2[\cos\vartheta(0)]\overline{f^{2,m}_{n,k}(t)}\big\rangle$ so that $c^{2,0}_{0,0}(t) \equiv C_2(t)$.

In order to solve the hierarchy of moment equations so obtained, we introduce a supercolumn vector $\mathbf{C}_n(t)$ comprising five subvectors $\mathbf{c}^{2,m}_{n-1}(t)$, equation (40), with $m = 0$, $\pm 1, \pm 2$. Then the hierarchy of equations for $c^{2,m}_{n,k}(t)$ equations (41)–(45) can be transformed into the matrix three-term differential-recurrence equation (29), where

$$\mathbf{Q}_n^- = \begin{pmatrix} 0 & \mathbf{q}_n^- & 0 & 0 & 0 \\ 0 & 0 & -\mathbf{p}_n^- & 0 & 0 \\ 0 & \mathbf{p}_n^- & 0 & 0 & 0 \\ 0 & \mathbf{v}_n^- & 0 & 0 & -2\mathbf{p}_n^- \\ 0 & 0 & \mathbf{v}_n^- & 2\mathbf{p}_n^- & 0 \end{pmatrix}$$

$$\mathbf{Q}_n^+ = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 \\ 3\mathbf{q}_n^+ & 0 & -\mathbf{p}_n^+ & \mathbf{v}_n^+ & 0 \\ 0 & \mathbf{p}_n^+ & 0 & 0 & \mathbf{v}_n^+ \\ 0 & 0 & 0 & 0 & -2\mathbf{p}_n^+ \\ 0 & 0 & 0 & 2\mathbf{p}_n^+ & 0 \end{pmatrix}$$

$$\mathbf{Q}_n = \begin{pmatrix} \mathbf{q}_n^0 & \mathbf{I}_n/2 & 0 & 0 & 0 \\ 6(\mathbf{r}_n - \mathbf{I}_n) & \mathbf{q}_n^1 & 0 & \mathbf{I}_n & 0 \\ 0 & 0 & \mathbf{q}_n^1 & 0 & \mathbf{I}_n \\ 0 & \mathbf{r}_n & 0 & \mathbf{q}_n^0 & 0 \\ 0 & 0 & \mathbf{r}_n & 0 & \mathbf{q}_n^0 \end{pmatrix}.$$

Here the submatrices $\mathbf{p}_n^\pm$, $\mathbf{q}_n^\pm$, $\mathbf{r}_n$ and $\mathbf{q}_n^M$ are given by equations (30)–(35) and

$$\mathbf{v}_n^- = -4 \begin{pmatrix} n & 0 & \cdots & 0 \\ 0 & n-1 & \cdots & 0 \\ \vdots & \vdots & \ddots & \vdots \\ 0 & 0 & \cdots & 2 \\ 0 & 0 & \cdots & 0 \end{pmatrix}_{n\times(n-1)}$$

$$\mathbf{v}_n^+ = \frac{1}{4} \begin{pmatrix} 1 & 0 & \cdots & 0 & 0 \\ 0 & 1 & \cdots & 0 & 0 \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & 0 \end{pmatrix}_{n\times(n+1)}.$$

The exact solution for the Laplace transform $\tilde{\mathbf{C}}_1(s)$ is then given by the matrix continued fraction, namely

$$\tilde{\mathbf{C}}_1(s) = \eta \cfrac{\mathbf{I}_5}{\eta s\mathbf{I}_5 - \mathbf{Q}_1 - \mathbf{Q}_1^+ \cfrac{\mathbf{I}_{10}}{\eta s\mathbf{I}_{10} - \mathbf{Q}_2 - \mathbf{Q}_2^+ \cfrac{\mathbf{I}_{15}}{\eta s\mathbf{I}_{15} - \mathbf{Q}_3 \,{\cdot\cdot\cdot}}\mathbf{Q}_3^-}\mathbf{Q}_2^-}\mathbf{C}_1(0)] \tag{46}$$
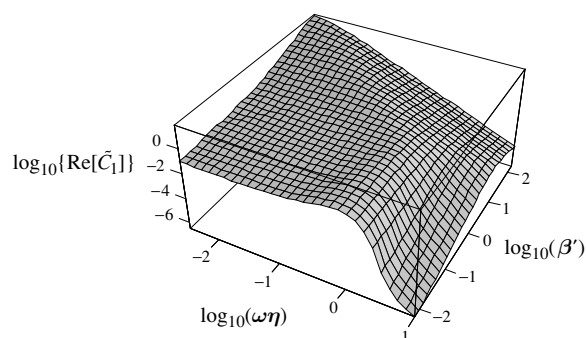
Figure 1. 3D-plot of $\log_{10}\{\mathrm{Re}[\tilde{C}_1]\}$ as a function of $\log_{10}(\omega\eta)$ and $\log_{10}(\beta')$ for spherical top molecules ($I = I_z$) and $\beta' = \beta'_z$.

with initial conditions

$$\mathbf{C}_1(0) = \begin{pmatrix} 1/5 \\ 0 \\ 0 \\ 0 \\ 0 \end{pmatrix} \qquad \text{and} \qquad \mathbf{C}_n(0) = \mathbf{0} \qquad \text{for all} \quad n \geqslant 2.$$

As an example the results of numerical calculations for linear ($I_z = 0$) molecules based on the above matrix continued fraction solution have been compared with those of [20] presented in terms of ordinary continued fractions, namely

$$\tilde{C}_2(s) = \cfrac{\eta/5}{\eta s + \cfrac{3}{\eta s + \beta' + \cfrac{5}{\eta s + 2\beta'} - \cfrac{b_0}{\eta s + a_1 - \cfrac{b_1}{\eta s + a_2 - \cfrac{b_2}{\eta s + a_3 - \ddots}}}}} \tag{47}$$

where

$$a_n = (2n+1)\beta' + \frac{4n+3}{2n\beta' + \eta s} + \frac{4n+5}{2(n+1)\beta' + \eta s}$$

and

$$b_n = \frac{16(n+1)(n+2)}{[2(n+1)\beta' + \eta s]^2}.$$

The numerical calculations show that both matrix and ordinary continued fraction solutions yield the same results. In order to illustrate this, the 3D-plots of $\log_{10}\{\mathrm{Re}[\tilde{C}_1]\}$ and of $\log_{10}\{\mathrm{Re}[\tilde{C}_2]\}$ versus $\log_{10}(\omega\eta)$ and $\log_{10}(\beta')$ for spherical top molecules ($I = I_z$) and isotropic diffusion ($\beta' = \beta'_z$) are shown in figures 1 and 2, respectively.

5. Discussion of the results

The matrix continued fraction solutions we have obtained are very useful in computation (various algorithms for calculating matrix continued fractions are discussed in [22], ch 9). The calculations have shown that for $\beta', \beta'_z > 0.005$, the matrix continued fraction involved
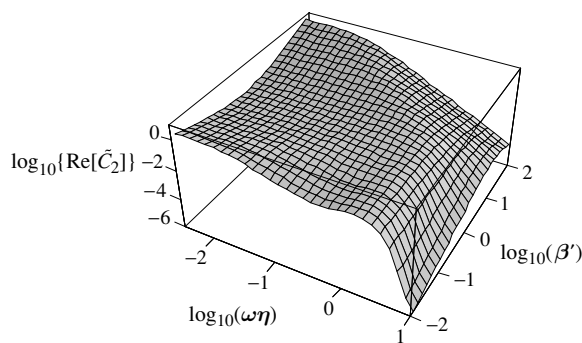
Figure 2. 3D-plot of $\log_{10}\{\mathrm{Re}[\tilde{C}_2]\}$ as a function of $\log_{10}(\omega\eta)$ and $\log_{10}(\beta')$ for spherical top molecules ($I = I_z$) and $\beta' = \beta'_z$.

converges very rapidly, thus 10–60 downward iterations in evaluating these matrix continued fractions are enough to arrive at not less than six significant digits in the majority of cases (with decreasing β' and β'_z, a number of iterations increases).

For very small β', β'_z (<0.001), the numerical procedure may become unstable. However, in this very low damping limit and $\omega\beta' > 10$, the $\tilde{C}_l(\mathrm{i}\omega)$ are very close to those of the free rotation model $\tilde{C}_l^{FR}(\mathrm{i}\omega)$ (β', $\beta'_z \equiv 0$) [24], namely

$$\tilde{C}_l(\mathrm{i}\omega) \approx \tilde{C}_l^{FR}(\mathrm{i}\omega)$$

$$= -\frac{\mathrm{i}}{\omega} C_l^{FR}(\infty) + 4\eta\sqrt{1+b} \sum_{m=1}^{l} m^{-1} \int_0^1 \left| d_{0,m}^l[\cos^{-1}(x)] \right|^2 F\left[\mathrm{i}\frac{\eta\omega}{m}\sqrt{1+bx^2}\right] \mathrm{d}x$$

(48)

where $b = I/I_z - 1$,

$$C_l^{FR}(\infty) = \sqrt{1+b} \int_0^1 \frac{P_l^2(x)}{\sqrt{1+bx^2}} \mathrm{d}x \qquad F(z) = z\{1 - \sqrt{\pi}z \exp(z^2)[1 - \mathrm{erf}(z)]\}.$$

$\mathrm{erf}(z)$ is the error function [25] and the $d_{M,M'}^l(\vartheta)$ are functions familiar in the theory of angular momentum; explicit equations for $d_{M,M'}^l(\vartheta)$ are given, e.g., in [25], p 78. One has, for example,

$$d_{0,0}^l[\cos^{-1}(x)] = P_l(x) \qquad d_{0,\pm 1}^1[\cos^{-1}(x)] = \pm\frac{\sqrt{1-x^2}}{\sqrt{2}}$$

$$d_{0,\pm 1}^2[\cos^{-1}(x)] = \pm\sqrt{\frac{3}{2}}x\sqrt{1-x^2} \qquad d_{0,\pm 2}^2[\cos^{-1}(x)] = \frac{1}{2}\sqrt{\frac{3}{2}}(1-x^2) \quad \text{etc.}$$

In the opposite (high damping) limit, $\beta' \to \infty$, the form of the spectrum $\tilde{C}_l(\mathrm{i}\omega)$ becomes Lorentzian (see figures 1 and 2) and coincides with that of the noninertial rotational diffusion Debye (model) [3], namely

$$\tilde{C}_l^D(\mathrm{i}\omega) = \frac{C_l(0)}{\mathrm{i}\omega + l(l+1)/(2\tau_D)}$$

(49)

where $\tau_D = \eta\beta' = \zeta/(2k_BT)$ is the (Debye) relaxation time.

The matrix continued fraction solution we have obtained is not only useful for numerical calculations, but also fruitful in analysis using symbolic calculations in the MATHEMATICA program. For example, in the high damping limit ($\beta' \gg 1$) and isotropic diffusion ($\beta'_z = \beta'$),

we obtain the following Taylor series expansion for the orientational relaxation times $\tau_1 = \tilde{C}_1(0)/C_1(0)$ and $\tau_2 = \tilde{C}_2(0)/C_2(0)$ (equation (12) for $n = 1, 2$) of the symmetric top:

$$\frac{\tau_1}{\tau_D} = 1 + \frac{1 + B + B^2}{1 + B}\gamma - \frac{2(2 + 5B + 4B^2 + B^3 + 3B^5)}{3(1 + B)^2(2 + B)}\gamma^2 + O(\gamma^3). \qquad (50)$$

and

$$\frac{3\tau_2}{\tau_D} = 1 + \frac{5 + 5B + B^2}{1 + B}\gamma - \frac{2(32 + 80B + 76B^2 + 46B^3 + 12B^4 + 3B^5)}{3(1 + B)^2(2 + B)}\gamma^2 + O(\gamma^3). \qquad (51)$$

Here $\gamma = 1/(2\beta'^2)$ is the inertial (Sack's [6]) parameter. For spherical tops ($B = 1$) and linear rotators ($B = 0$), equations (50) and (51) reduce to known results, respectively [1],

$$\frac{\tau_1}{\tau_D} = 1 + \frac{3}{2}\gamma - \frac{5}{6}\gamma^2 + O(\gamma^3) \qquad (52)$$

$$\frac{3\tau_2}{\tau_D} = 1 + \frac{11}{2}\gamma - \frac{83}{6}\gamma^2 + O(\gamma^3) \qquad (53)$$

and

$$\frac{\tau_1}{\tau_D} = 1 + \gamma - \frac{2}{3}\gamma^2 + O(\gamma^3) \qquad (54)$$

$$\frac{3\tau_2}{\tau_D} = 1 + 5\gamma - \frac{32}{3}\gamma^2 + O(\gamma^3). \qquad (55)$$

Results of our calculations of the spectra $\tilde{C}_1(i\omega)$ and $\tilde{C}_2(i\omega)$ and the orientational relaxation times τ_1 and τ_2 show that these quantities depend on the frictional anisotropy (β'/β'_z) and the shape parameter $B = I_z/I$ and agree in all respects with those obtained using the Fokker–Planck equation [1, 10]. As far as comparison with experimental data is concerned, the Langevin–Fokker–Planck model is suitable only for the explanation of the rotational motion of small molecules (such as N_2O, CF_4, and so on) in liquids [3, 11]. Here, the model reasonably describes experimental data on infrared absorption, Raman scattering, nuclear magnetic relaxation, etc (see, e.g., [3, 9, 11], where a detailed comparison with experiments is given); however, it is not applicable [2] to liquids comprised larger molecules, where the rotational motion is more hindered and has a librational character. The failure of the Langevin–Fokker–Planck model as well as all other inertia corrected Debye-type models [3] to account for the high-frequency molecular librations in neat liquids even though they explain the return to transparency at high frequencies is to be expected [2] in view of the assumption made in the theory that all electrical interactions between dipoles may be neglected.

To conclude we have derived an infinite hierarchy of differential-recurrence equations (23) and (24) for the statistical moments governing the inertial Brownian motion of a symmetric top molecule freely rotating in space by using the Langevin equation method. We have also obtained exact analytical solutions (in terms of matrix continued fractions) of this hierarchy for the one-sided Fourier transforms of the first, $C_1(t)$, and the second, $C_2(t)$, order equilibrium orientational correlation functions. The problem at hand provides a convenient benchmark solution for the method as it may also be solved using other methods (cf Sack's equation (39)). The method of solution of orientational relaxation problems, which we have proposed, is quite general because it is based on the concept of the equation of motion of an observable which in turn is based on the dynamical (Langevin) theory [19] of the Brownian motion. The attractive feature of the dynamical method is that it allows one to compute directly from the dynamical equations of motion the spectra of the equilibrium CFs $\tilde{C}_l(i\omega)$ taking account of the effect of molecular inertia on orientational relaxation in liquids. The major

advantage that the dynamical (Langevin) method has over the Fokker–Planck equation is that it avoids both the derivation of this equation for the distribution function $W(\vartheta, \omega_x, \omega_y, \omega_z, t)$ in phase space, which for the problem in question is [12]

$$\frac{\partial W}{\partial t} + \omega_x \frac{\partial W}{\partial \vartheta} + \left(\omega_y \cot \vartheta - \frac{I_z}{I}\omega_z\right)\left(\omega_y \frac{\partial W}{\partial \omega_x} - \omega_x \frac{\partial W}{\partial \omega_y}\right) = \frac{\zeta}{I}\frac{\partial}{\partial \omega_x}\left(\omega_x W + \frac{k_B T}{I}\frac{\partial W}{\partial \omega_x}\right)$$

$$+ \frac{\zeta}{I}\frac{\partial}{\partial \omega_y}\left(\omega_y W + \frac{k_B T}{I}\frac{\partial W}{\partial \omega_y}\right) + \frac{\zeta_z}{I_z}\frac{\partial}{\partial \omega_z}\left(\omega_z W + \frac{k_B T}{I_z}\frac{\partial W}{\partial \omega_z}\right)$$

and also the complex mathematical manipulations associated with the separation of variables in that equation, which combine to obscure the physics underlying the problem. The method developed is essential for the solution of problems involving spatial rotation in a potential as recurrence relation involving more than two numbers will always occur.

Acknowledgment

Appendix A. Derivation of differential-recurrence equations for $\overline{f_{n,k}^{l,m}(t)}$

In order to derive the hierarchy of equations for average values of $\overline{f_{n,k}^{l,m}(t)}$, we first note that

$$\overline{\frac{\mathrm{d}}{\mathrm{d}t}f_{n,k}^{l,m}(t)} = \overline{P_l^{|m|}\frac{\mathrm{d}}{\mathrm{d}t}s_{n,k}^m + s_{n,k}^m\frac{\mathrm{d}}{\mathrm{d}t}P_l^{|m|}}.$$

For arbitrary l and $m = 0$, we can evaluate the two terms on the right-hand side of the above equation as follows:

$$\overline{s_{n,k}^0[\omega_x(t), \omega_y(t), \omega_z(t)]\frac{\mathrm{d}}{\mathrm{d}t}P_l[\cos\vartheta(t)]}$$

$$= \overline{\omega_x(t)s_{n,k}^0[\omega_x(t), \omega_y(t), \omega_z(t)]P_l^1[\cos\vartheta(t)]}$$

$$= \frac{1}{2\eta}P_l^1 H_k^z \sum_{q=0}^{n}\frac{\left(H_{2n-2q+1}^x + 4(n-q)H_{2n-2q-1}^x\right)H_{2q}^y}{q!(n-q)!} = \frac{1}{2\eta}P_l^1\left(s_{n,k}^1 + 4s_{n-1,k}^1\right)$$

(A1)

and

$$\overline{P_l[\cos\vartheta(t)]\frac{\mathrm{d}}{\mathrm{d}t}s_{n,k}^0[\omega_x(t), \omega_y(t), \omega_z(t)]} = \overline{P_l[\cos\vartheta(t)]\sum_{q=0}^{n}\frac{4\eta}{q!(n-q)!}}$$

$$\times\left[(n-q)H_{2n-2q-1}^x(t)H_{2q}^y(t)H_k^z(t)\dot\omega_x(t) + q H_{2n-2q}^x(t)H_{2q-1}^y(t)H_k^z(t)\dot\omega_y(t)\right.$$

$$\left.+ \frac{\eta_z k}{2\eta}H_{2n-2q}^x(t)H_{2q}^y(t)H_{k-1}^z(t)\dot\omega_z(t)\right]$$

$$= P_l[\cos\vartheta(t)]\sum_{q=0}^{n}\frac{4\eta}{q!(n-q)!}\left\{(n-q)H_{2n-2q-1}^x(t)H_{2q}^y(t)\right.$$

$$\times\overline{\left[-\omega_y(t)\left(\frac{I_z}{I}\omega_z(t) - \omega_y(t)\cot\vartheta\right) - \frac{\zeta}{I}\omega_x(t) + \frac{\lambda_x(t)}{I}\right]}$$

$$+ q H_{2n-2q}^x(t) H_{2q-1}^y(t) \left[\omega_x(t) \left(\frac{I_z}{I} \omega_z(t) - \omega_y(t) \cot \vartheta \right) - \frac{\zeta}{I} \omega_y(t) + \frac{\lambda_y(t)}{I} \right]$$

$$+ \frac{\eta_z k}{2\eta} H_{2n-2q}^x(t) H_{2q}^y(t) H_{k-1}^z(t) \left[-\frac{\zeta_z}{I_z} \omega_z(t) + \frac{\lambda_z(t)}{I_z} \right] \Bigg\} = -(2n\beta + k\beta_z) P_l s_{n,k}^0$$

(A2)

where $H_n^j(t) \equiv H_n[\eta \omega_j(t)] (j = x, y, z)$ and $\dot{\omega}_x(t)$, $\dot{\omega}_y(t)$ and $\dot{\omega}_z(t)$ are given by equations (7)–(9). In order to simplify equations (A1) and (A2), we have used the identities [23]

$$\frac{\partial}{\partial \vartheta} P_l(\cos \vartheta) = P_l^1(\cos \vartheta)$$

(A3)

$$\frac{\mathrm{d}}{\mathrm{d}x} H_n(x) = 2n H_{n-1}(x)$$

(A4)

$$H_{n+1}(x) = 2x H_n(x) - 2n H_{n-1}(x)$$

(A5)

and the relations from Stratonovich calculus [19, 20]

$$\overline{\lambda_i(t) E[\vartheta(t), \omega_j(t), \omega_k(t)] H_n[\eta \omega_i(t)]} = \frac{\zeta n}{\eta} E(\vartheta, \omega_j, \omega_k) H_{n-1}(\eta \omega_i)$$

(A6)

where E is an arbitrary function and $i, j, k = x, y, z \, (i \neq j \neq k)$. Equation (A6) follows from Isserlis's theorem and is given in appendices A–C of [19]. On combining equations (A1) and (A2), one can obtain equation (23).

In like manner, we have for $m \neq 0$

$$\overline{s_{n,k}^{2m-M}[\omega_x(t), \omega_y(t), \omega_z(t)] \frac{\mathrm{d}}{\mathrm{d}t} P_l^{|2m-M|}[\cos \vartheta(t)]}$$

$$= \omega_x(t) s_{n,k}^{2m-M}[\omega_x(t), \omega_y(t), \omega_z(t)] \frac{\partial}{\partial \vartheta} P_l^{|2m-M|}[\cos \vartheta(t)]$$

$$= \frac{1}{4\eta} \left[P_l^{|2m-M|+1}(\cos \vartheta) - (l + |2m - M|)(l + 1 - |2m - M|) P_l^{|2m-M|-1}(\cos \vartheta) \right]$$

$$\times H_k^z \sum_{q=0}^{n} \frac{r_{2m-M}(n,q)}{q!(n-q)!} \left[H_{2n-2q+M-\varepsilon_m+1}^x \right.$$

$$\left. + 2(2n - 2q + M - \varepsilon_m) H_{2n-2q+M-\varepsilon_m-1}^x \right] H_{2q+\varepsilon_m}^y$$

(A7)

and

$$\overline{P_l^{|2m-M|}[\cos \vartheta(t)] \frac{\mathrm{d}}{\mathrm{d}t} s_{n,k}^{2m-M}[\omega_x(t), \omega_y(t), \omega_z(t)]} = -[(2n + M)\beta + k\beta_z] P_l^{|2m-M|} s_{n,k}^{2m-M}$$

$$+ \sum_{q=0}^{n} \frac{(n-q)(2 + \varepsilon_m/(q+1)) r_{2m-M}(n, q+1) - (2n - 2q + M - \varepsilon_m) r_{2m-M}(n, q)}{q!(n-q)!}$$

$$\times \left\{ \frac{1}{4\eta |2m - M|} \left[P_l^{|2m-M|+1}(\cos \vartheta) + (l + |2m - M|)(l + 1 - |2m - M|) P_l^{|2m-M|-1}(\cos \vartheta) \right] \right.$$

$$\times H_{2n-2q+M-1-\varepsilon_m}^x \left(H_{2q+2+\varepsilon_m}^y + 2(2q + 1 + \varepsilon_m) H_{2q+\varepsilon_m}^y \right) H_k^z$$

$$\left. + \frac{I_z}{I} \frac{1}{2\eta_z} P_l^{|2m-M|} H_{2n-2q+M-1-\varepsilon_m}^x H_{2q+1+\varepsilon_m}^y \left(H_{k+1}^z + 2k H_{k-1}^z \right) \right\}.$$

(A8)

Here equations (A3)–(A6) and the following relations of the associated Legendre functions have been used [23]:

$$2\frac{\partial}{\partial \vartheta} P_l^m = P_l^{m+1} - (l+m)(l-m+1)P_l^{m-1}$$

$$2m \cot \vartheta P_l^m = -P_l^{m+1} - (l+m)(l-m+1)P_l^{m-1}$$

and

$$(2l+1)\sin \vartheta P_l^m = P_{l-1}^{m+1} - P_{l+1}^{m+1} = (l-m+1)(l-m+2)P_{l+1}^{m-1} - (l+m-1)(l+m)P_{l-1}^{m-1}.$$

Noting equations (A7) and (A8), we have equations (23) and (24).

Appendix B. Sack's continued fraction solution for sphere

Sack [6] obtained a solution for the dielectric (first-order) response in terms of a scalar continued fraction (his equation (3.19)). Unfortunately, no details of the derivation have been given; moreover, a misprint in his equation exists. This has led to some confusion in the literature as Sack's solution was used as printed, see, e.g., [1, 9]. Here, a detailed derivation of Sack's continued fraction solution is given. In the notation of Sack [6], the dynamics of an assembly of spherical top molecules is governed by the recurrence equations:

$$i\omega' a_0 + 2b_1 = i\omega' \tag{B1}$$

$$(i\omega' + n)a_n + (n+2)b_{n+1} - \gamma b_{n-1} = 0 \tag{B2}$$

$$\left[i\omega' + n + \frac{2\gamma}{(n+3)(i\omega' + n + 1)}\right]b_n + \left(n+2 - \frac{2}{n+3}\right)a_{n+1} - \gamma a_{n-1} = 0 \tag{B3}$$

where $\gamma = 1/(2\beta'^2)$ and $\omega' = I\omega/\zeta$. One can formally solve equations (B1)–(B3) for a_0 as

$$a_0 = \cfrac{i\omega'}{i\omega' + \cfrac{2}{i\omega' + 1 + \cfrac{\gamma}{2(i\omega' + 2)}\left[\gamma - \left(3 - \frac{1}{2}\right)\frac{a_2}{a_0}\right]}} \tag{B4}$$

where the infinite continued fraction a_2/a_0 must be evaluated from the following recurrence equation:

$$\frac{a_n}{a_{n-2}} = \cfrac{\cfrac{\gamma^2}{i\omega' + n - 1 + \cfrac{2\gamma}{(n+2)(i\omega' + n)}}}{i\omega' + n + \cfrac{\gamma\left(n+1 - \cfrac{2}{n+2}\right)}{i\omega' + n - 1 + \cfrac{2\gamma/(n+2)}{i\omega' + n}} + \cfrac{(n+2)\left[\gamma - \left(n+3 - \cfrac{2}{n+4}\right)\cfrac{a_{n+2}}{a_n}\right]}{i\omega' + n + 1 + \cfrac{2\gamma/(n+4)}{i\omega' + n + 2}}} \tag{B5}$$

($n \geqslant 2$). One may see by inspection that the continued fraction (B5) differs from that given by Sack [6]. However, equation (B5) can be rearranged as follows:

$$Z_n = \cfrac{\gamma n}{i\omega' + n - 1 + \cfrac{2\gamma/(n+2)}{i\omega' + n} + \cfrac{\gamma n(n+3)/(n+2)}{i\omega' + n + Z_{n+2}}} \tag{B6}$$

where Z_n is defined as

$$Z_n = \cfrac{n}{i\omega' + n - 1 + \cfrac{2\gamma}{(n+2)(i\omega' + n)}}\left[\gamma - \left(n+1 - \frac{2}{n+2}\right)\frac{a_n}{a_{n-2}}\right]. \tag{B7}$$

Thus, we obtain from equations (B4) and (B6)

$$a_0 = \frac{i\omega'}{i\omega' + Z_2} =$$

$$\cfrac{i\omega'}{i\omega' + \cfrac{2\gamma}{1 + i\omega' + \cfrac{\gamma}{2(2 + i\omega')} + \cfrac{(3 - 1/2)\gamma}{2 + i\omega' + \cfrac{4\gamma}{3 + i\omega' + \cfrac{\gamma}{3(4 + i\omega')} + \cfrac{(5 - 1/3)\gamma}{4 + i\omega' + \cfrac{6\gamma}{5 + i\omega' + \cfrac{\gamma}{4(6 + i\omega')} + \cdots}}}}}$$

$$\text{(B8)}$$

that is Sack's result ([6], equation (3.19)) with the corrected misprint. On noting that $\tilde{C}_1(i\omega) = a_0/(3i\omega)$, equation (B8) yields equation (39).

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