CORRELATION FUNCTIONS FOR SPHERICAL HARMONICS RESULTING FROM ROTATIONAL BROWNIAN MOTION OF A LINEAR MOLECULE

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ABSTRACT

The autocorrelation functions for spherical harmonics arising from the rotational Brownian motion of the linear model of a polar molecule are calculated by using Langevin equations and the stochastic averaging method employed by Ford, Lewis and McConnell for the analogous problem with the spherical model.

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1. Introduction

The rotational Brownian motion, with inclusion of inertial effects, of the linear model of a polar molecule - also called the needle model - was first investigated in detail by Sack [1957]. He constructed a Fokker-Planck-Kramers equation in the space of the two angles specifying the orientation of the molecule and of their related angular velocities. Sack expressed the steady state linear response to an alternating field as a continued fraction which is a function of the frequency, the friction constant β and the moment of inertia I of the molecule about a line perpendicular to it through its middle point.

The steady state response is related to the autocorrelation function of the cosine of the angle between the axis of the dipole and the direction of the electric field through the Kubo equation [cf. Scaife 1971 section 2]. In the present paper autocorrelation functions for spherical harmonics resulting from the motion of the molecule are expressed as exponentials, the exponents being series in power of $kT/I\beta^2$ up to the third power. The method of investigation is rather similar to that adopted for the rotational Brownian motion of a sphere in Ford, Lewis and McConnell 1976, to be referred to briefly as FLM. However, the absence of spherical symmetry precludes the use of the graphical method and for this reason it would be tedious to take the calculation as far as terms proportional to $(kT/I\beta^2)^4$.

The motion is investigated by employing Euler-Langevin equations referred to coordinate axes rotating with the needle, which is regarded as an extremely thin spheroid with zero component of angular velocity about its line of symmetry. Correlation functions for components of angular velocity perpendicular to this line are given, and they lead to the autocorrelation functions for spherical harmonics. The results are in agreement with that of Sack, when the harmonic is the cosine function.

2. Equations of motion of the linear rotator

We picture the rotator as a body with zero angular velocity about its axis. We take rotating coordinate axes with origin at the centre of the body, the third axis being along the line of symmetry and the other two being perpendicular to the line and to one another. We denote by I the moment of inertia about the first and second axes. The Euler-Langevin equations of motion are

$$I\dot{\omega}_1 = -I\beta\omega_1 + IA_1(t)$$
$$I\dot{\omega}_2 = -I\beta\omega_2 + IA_2(t), \tag{1}$$

where $IA_1(t)$, $IA_2(t)$ are the components of the random driving couple due to the surrounding medium and the frictional couple is $I\beta$ times the angular velocity. Equations (1) simplify to

$$\dot{\omega}_1 = -\beta\omega_1 + A_1(t), \quad \dot{\omega}_2 = -\beta\omega_2 + A_2(t). \tag{2}$$

$A_1(t)$, $A_2(t)$ are Gaussian white noise terms satisfying

$$\langle A_i(t_k)\, A_j(t_l)\rangle = c^2\delta_{ij}\,\delta(t_k - t_l), \quad (i,j = 1,2)$$
$$\langle A_i(t)\rangle = 0, \qquad (i = 1,2)$$

the constant c^2 being the same for i = 1 and i = 2 on account of the symmetry of the body. We assume that the Brownian motion has reached a steady state. Then by adapting the Ornstein-Uhlenbeck theory [cf. Lewis, McConnell and Scaife 1976 eq. (12) and (14)] we can write for the correlation function of the components of angular velocity

$$\langle \omega_i(t_k)\,\omega_j(t_l)\rangle = \frac{kT}{I}\,\delta_{ij}\,e^{-\beta|t_k - t_l|}. \tag{3}$$

3. Averaging method for the rotation operator

Let us write

$$R(t,0) = e^{-i\alpha(t)J_z}\,e^{-i\beta(t)J_y}\,e^{-i\gamma(t)J_z}, \tag{4}$$

which is the operator for the rotation of coordinate axes [cf. Rose 1957 p.50]. Here J_x, J_y, J_z are the angular momentum operators divided by $\hbar$ and $\alpha(t)$, $\beta(t)$, $\gamma(t)$ are the Euler angles of the rotated system. We choose these angles such that $\alpha(0) = \beta(0) = \gamma(0) = 0$, and thence R(0, 0) is the identity operator $\mathbb{1}$. We take the rotating axes to be the moving axes chosen in the previous section for the linear rotator. The m m'-element of R(t,0) for the basis consisting of the spherical harmonics $Y_{js}(\beta(0), \alpha(0))$ with s = j, j-1, ..., -j is written $D^j_{mm'}(\alpha(t), \beta(t), \gamma(t))$ and

$$D^{j*}_{m0}(\alpha(t), \beta(t), \gamma(t)) = \sqrt{\frac{4\pi}{2j+1}}\,Y_{jm}(\beta(t), \alpha(t))$$
$$D^j_{00}(\alpha(t), \beta(t), \gamma(t)) = P_j(\cos\beta(t)) \tag{5}$$

The operator R(t,0) satisfies the relation

$$\frac{dR(t,0)}{dt} = i\left(J_1\omega_1(t) + J_2\omega_2(t)\right)R(t,0), \tag{6}$$

where J_1, J_2, J_3 are the angular momentum operators divided by $\hbar$ for the rotating coordinate system. The stochastic operator $i\left(J_1\omega_1(t) + J_2\omega_2(t)\right)$ satisfies assumptions 1 and 3 of FLM page 121 for the present problem. This is sufficient to permit us to write

$$\frac{d\langle R(t,0)\rangle}{dt} = \left(\Omega^{(2)}(t) + \Omega^{(4)}(t) + \Omega^{(6)}(t) + \dots\right)\langle R(t,0)\rangle, \tag{7}$$

where on account of the presence of the imaginary coefficient in (6) we have from equations (25), (26) and (30) of FLM

$$\Omega^{(2)}(t_1) = -\int_0^{t_1} dt_2 \langle 12 \rangle \tag{8}$$

$$\Omega^{(4)}(t_1) = \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \{\langle 1234 \rangle - \langle 12 \rangle\langle 34 \rangle - \langle 13 \rangle\langle 24 \rangle - \langle 14 \rangle\langle 23 \rangle\} \tag{9}$$

$$\begin{aligned}\Omega^{(6)}(t_1) = -\int_0^{t_1} dt_2 \int_0^{t_2} dt_3 \int_0^{t_3} dt_4 \int_0^{t_4} dt_5 \int_0^{t_5} dt_6\, [&\langle 123456 \rangle - \langle 12 \rangle\langle 3456 \rangle - \langle 13 \rangle\langle 2456 \rangle \\ &- \langle 14 \rangle\langle 2356 \rangle - \langle 15 \rangle\langle 2346 \rangle - \langle 16 \rangle\langle 2345 \rangle - \langle 1234 \rangle\langle 56 \rangle - \langle 1235 \rangle\langle 46 \rangle \\ &- \langle 1245 \rangle\langle 36 \rangle - \langle 1345 \rangle\langle 26 \rangle - \langle 1236 \rangle\langle 45 \rangle - \langle 1246 \rangle\langle 35 \rangle - \langle 1346 \rangle\langle 25 \rangle \\ &- \langle 1256 \rangle\langle 34 \rangle - \langle 1356 \rangle\langle 24 \rangle - \langle 1456 \rangle\langle 23 \rangle \\ &+ 2\langle 12 \rangle\langle 34 \rangle\langle 56 \rangle + 2\langle 12 \rangle\langle 35 \rangle\langle 46 \rangle + 2\langle 12 \rangle\langle 36 \rangle\langle 45 \rangle \\ &+ 2\langle 13 \rangle\langle 24 \rangle\langle 56 \rangle + 2\langle 13 \rangle\langle 25 \rangle\langle 46 \rangle + 2\langle 13 \rangle\langle 26 \rangle\langle 45 \rangle \\ &+ 2\langle 14 \rangle\langle 23 \rangle\langle 56 \rangle + 2\langle 14 \rangle\langle 25 \rangle\langle 36 \rangle + 2\langle 14 \rangle\langle 26 \rangle\langle 35 \rangle \\ &+ 2\langle 15 \rangle\langle 23 \rangle\langle 46 \rangle + 2\langle 15 \rangle\langle 24 \rangle\langle 36 \rangle + 2\langle 15 \rangle\langle 26 \rangle\langle 34 \rangle \\ &+ 2\langle 16 \rangle\langle 23 \rangle\langle 45 \rangle + 2\langle 16 \rangle\langle 24 \rangle\langle 35 \rangle + 2\langle 16 \rangle\langle 25 \rangle\langle 34 \rangle] ,\end{aligned} \tag{10}$$

In the above brackets an integer ℓ is an abbreviation for $J_1\omega_1(t_\ell)+J_2\omega_2(t_\ell)$ so that, for example,

$$\begin{aligned}\langle 12 \rangle &= \langle J_1\omega_1(t_1)+J_2\omega_2(t_1)\rangle\langle J_1\omega_1(t_2)+J_2\omega_2(t_2)\rangle \\ &= \frac{kT}{I}\left(J_1^2+J_2^2\right) e^{-\beta(t_1-t_2)} ,\end{aligned} \tag{11}$$

where we use (3) and the knowledge that in the above integrals $t_1 \geq t_2 \geq t_3 \geq t_4 \geq t_5 \geq t_6$. It is clear that

$$\langle 12 \rangle\langle 34 \rangle = \langle 34 \rangle\langle 12 \rangle$$

etc., and this has allowed us to combine terms with the structure $\langle\cdot\cdot\rangle\langle\cdot\cdot\rangle\langle\cdot\cdot\rangle$ in (10). On the other hand the absence of J_3 in (10) prevents the reduction of equations (26) and (30) of FLM to (29) and (31), respectively, which was possible for the rotating sphere.

4. Calculation of $\Omega^{(2)}(t_1)$, $\Omega^{(4)}(t_1)$, $\Omega^{(6)}(t_1)$

We proceed to calculate $\Omega^{(2)}(t_1), \Omega^{(4)}(t_1), \Omega^{(6)}(t_1)$. From (8) and (11)

$$\Omega^{(2)}(t_1) = -\frac{kT}{I}\left(J_1^2+J_2^2\right)\int_0^{t_1} e^{-\beta(t_1-t_2)} dt_2 . \tag{12}$$

The J_1, J_2, J_3 satisfy the commutation relations

$$J_k J_\ell - J_\ell J_k = -i\sum_{n=1}^{3} \varepsilon_{k\ell n} J_n \tag{13}$$

$$J^2 = j(j+1)\,1 , \tag{14}$$

where

$$J^2 = J_1^2 + J_2^2 + J_3^2 \tag{15}$$

and $\varepsilon_{\ell\ell n}$ is the totally antisymmetric Levi Civita symbol. The - i appears on the right hand side of (13) because the J_k -operators refer to rotating axes [cf. Van Vleck 1951]. We adopt henceforth the convention that a repeated suffix is summed over 1 and 2 only, and so from (15)

$$J_k^2 = J^2 - J_3^2 . \tag{16}$$

While J^2 is a multiple of the identity operator, J_k^2 is not and this causes complications not present in the spherical top model. Since J^2 commutes with J_3, we shall endeavour to express all sums of products of J_k's that occur in future calculations in terms of J^2 and J_3^2. Thus we write (12) as

$$\Omega^{(2)}(t_1) = -\frac{kT}{I}\left(J^2-J_3^2\right)\int_0^{t_1} e^{-\beta(t_1-t_2)} dt_2 . \tag{17}$$

We examine the integral on the right hand side of (9). We have

$$\langle 1234\rangle = \langle J_i\omega_i(t_1)J_k\omega_k(t_2)J_\ell\omega_\ell(t_3)J_n\omega_n(t_4)\rangle$$
$$= \langle \omega_i(t_1)\omega_k(t_2)\omega_\ell(t_3)\omega_n(t_4)\rangle J_iJ_kJ_\ell J_n .$$

On using the well-known result for a continued product of an even number of centred Gaussian random variables we deduce that

$$\begin{aligned}\langle 1234\rangle &= \Big(\langle\omega_i(t_1)\omega_k(t_2)\rangle\langle\omega_\ell(t_3)\omega_n(t_4)\rangle+\langle\omega_i(t_1)\omega_\ell(t_3)\rangle\langle\omega_k(t_2)\omega_n(t_4)\rangle\\ &\quad+\langle\omega_i(t_1)\omega_n(t_4)\rangle\langle\omega_k(t_2)\omega_\ell(t_3)\rangle\Big)J_iJ_kJ_\ell J_n\\ &= \langle\omega_i(t_1)\omega_i(t_2)\rangle\langle\omega_k(t_3)\omega_k(t_4)\rangle J_i^2J_k^2\\ &\quad+\langle\omega_i(t_1)\omega_i(t_3)\rangle\langle\omega_k(t_2)\omega_k(t_4)\rangle J_iJ_kJ_iJ_k\\ &\quad+\langle\omega_i(t_1)\omega_i(t_4)\rangle\langle\omega_k(t_2)\omega_k(t_3)\rangle J_iJ_k^2J_i\end{aligned} \qquad (18)$$

on noting the Knonecker delta in (3). This equation then gives

$$\langle 1234\rangle = \left(\frac{kT}{I}\right)^2\left\{e^{-\beta(t_1-t_2+t_3-t_4)}J_i^2J_k^2+e^{-\beta(t_1+t_2-t_3-t_4)}\left(J_iJ_kJ_iJ_k+J_iJ_k^2J_i\right)\right\}.$$

From (11) we may deduce that

$$\langle 12\rangle\langle 34\rangle+\langle 13\rangle\langle 24\rangle+\langle 14\rangle\langle 23\rangle = \left(\frac{kT}{I}\right)^2\left\{e^{-\beta(t_1-t_2+t_3-t_4)}+2e^{-\beta(t_1+t_2-t_3-t_4)}\right\}J_i^2J_k^2,$$

and therefore

$$\langle 1234\rangle - \langle 12\rangle\langle 34\rangle - \langle 13\rangle\langle 24\rangle - \langle 14\rangle\langle 23\rangle$$
$$= \left(\frac{kT}{I}\right)^2 e^{-\beta(t_1+t_2-t_3-t_4)}\left(J_iJ_kJ_iJ_k+J_iJ_k^2J_i-2J_i^2J_k^2\right). \qquad (19)$$

To express sums of products of J_k's in terms of J^2 and J_3^2 it will be found helpful to use the following relations which are consequences of (13) and (16):

$$\begin{aligned} i(J_2J_3J_1-J_1J_3J_2) &= J^2-2J_3^2\\ J_kJ_\ell J_kJ_\ell &= (J^2-J_3^2)^2-J^2+2J_3^2\\ J_kJ_\ell^2J_k &= (J^2-J_3^2)^2-J^2+3J_3^2\\ J_kJ_3^2J_k &= J^2J_3^2-(J_3^2)^2+J^2-3J_3^2\\ J_3J_k^2J_3 &= J^2J_3^2-(J_3^2)^2\\ i(J_2J_3^3J_1-J_1J_3^3J_2) &= 3J^2J_3^2-4(J_3^2)^2+J^2-4J_3^2\\ J_kJ_3^4J_k &= J^2(J_3^2)^2-(J_3^2)^3+6J^2J_3^2-10(J_3^2)^2+J^2-5J_3^2 .\end{aligned}$$

It will follow from (9), (19) and (20) that

$$\Omega^{(4)}(t_1) = -\left(\frac{kT}{I}\right)^2(2J^2-5J_3^2)\int_0^{t_1}dt_2\int_0^{t_2}dt_3\int_0^{t_3}dt_4\, e^{-\beta(t_1+t_2-t_3-t_4)} .$$

Let us calculate $\Omega^{(6)}(t_1)$ from (10) in a similar manner. We employ th linking notation of FLM which means that, for example, we would write (18) as

$$\langle 1234\rangle = \langle 1234\rangle + \langle 1234\rangle + \langle 1234\rangle .$$

The linking indicates the members with J_k's whose subscripts are made equal before summing over the J_k's. We now write

$$\begin{aligned}\langle 123456\rangle &= \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle\\ &\quad+ \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle\\ &\quad+ \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle + \langle 123456\rangle .\end{aligned}$$

The calculations are simplified by noting that the five terms which have either 12 or 56 linked sum to

$$\langle 12\rangle\langle 3456\rangle + \langle 1234\rangle\langle 56\rangle - \langle 12\rangle\langle 34\rangle\langle 56\rangle .$$

The surviving terms add up to

$$\left(\frac{kT}{I}\right)^3 e^{-\beta(t_1+t_2-t_3+t_4-t_5-t_6)}\left(J_kJ_\ell J_kJ_nJ_\ell J_n+J_kJ_\ell J_kJ_n^2J_\ell+J_kJ_\ell^2J_nJ_kJ_n+J_kJ_\ell^2J_n^2J_k\right)$$
$$+\left(\frac{kT}{I}\right)^3 e^{-\beta(t_1+t_2+t_3-t_4-t_5-t_6)}\left(J_kJ_\ell J_nJ_kJ_\ell J_n+J_kJ_\ell J_nJ_kJ_nJ_\ell+J_kJ_\ell J_nJ_\ell J_kJ_n\right.$$
$$\left.+J_kJ_\ell J_n^2J_kJ_\ell+J_kJ_\ell J_nJ_\ell J_nJ_k+J_kJ_\ell J_n^2J_\ell J_k\right). \qquad (24)$$

After repeated applications of (20) it is found that (24) is equal to

$$\left(\frac{kT}{I}\right)^3 e^{-\beta(t_1+t_2-t_3+t_4-t_5-t_6)}\left[4(J^2-J_3^2)^3-8(J^2)^2+37J^2J_3^2-29(J_3^2)^2+4J^2-16J_3^2\right]$$
$$+\left(\frac{kT}{I}\right)^3 e^{-\beta(t_1+t_2+t_3-t_4-t_5-t_6)}\left[6(J^2-J_3^2)^3-18(J^2)^2+84J^2J_3^2-66(J_3^2)^2+20J^2-68J_3^2\right], \qquad (25)$$

so that $\langle 123456\rangle$ is the sum of the expressions (23) and (25).

We next calculate the sum of the $-\langle\bullet\bullet\rangle\langle\bullet\bullet\bullet\bullet\rangle$ and $-\langle\bullet\bullet\bullet\bullet\rangle\langle\bullet\bullet\rangle$ terms in the integrand on the right hand side of (10). Of the fifteen such terms two are cancelled by terms in (23). For the remaining thirteen we put

$$-\langle 13\rangle\langle 2456\rangle = -\langle 13\rangle\langle 24\rangle\langle 56\rangle - \langle 13\rangle\langle 2456\rangle - \langle 13\rangle\langle 2456\rangle$$
$$-\langle 14\rangle\langle 2356\rangle = -\langle 14\rangle\langle 23\rangle\langle 56\rangle - \langle 14\rangle\langle 2356\rangle - \langle 14\rangle\langle 2356\rangle$$
$$-\langle 15\rangle\langle 2346\rangle = -\langle 15\rangle\langle 23\rangle\langle 46\rangle - \langle 15\rangle\langle 2346\rangle - \langle 15\rangle\langle 2346\rangle$$
$$-\langle 16\rangle\langle 2345\rangle = -\langle 16\rangle\langle 23\rangle\langle 45\rangle - \langle 16\rangle\langle 2345\rangle - \langle 16\rangle\langle 2345\rangle$$
$$-\langle 1235\rangle\langle 46\rangle = -\langle 12\rangle\langle 35\rangle\langle 46\rangle - \langle 1235\rangle\langle 46\rangle - \langle 1235\rangle\langle 46\rangle$$
$$-\langle 1245\rangle\langle 36\rangle = -\langle 12\rangle\langle 45\rangle\langle 36\rangle - \langle 1245\rangle\langle 36\rangle - \langle 1245\rangle\langle 36\rangle \qquad (26)$$
$$-\langle 1345\rangle\langle 26\rangle = -\langle 13\rangle\langle 45\rangle\langle 26\rangle - \langle 1345\rangle\langle 26\rangle - \langle 1345\rangle\langle 26\rangle$$
$$-\langle 1236\rangle\langle 45\rangle = -\langle 12\rangle\langle 36\rangle\langle 45\rangle - \langle 1236\rangle\langle 45\rangle - \langle 1236\rangle\langle 45\rangle$$
$$-\langle 1246\rangle\langle 35\rangle = -\langle 12\rangle\langle 46\rangle\langle 35\rangle - \langle 1246\rangle\langle 35\rangle - \langle 1246\rangle\langle 35\rangle$$
$$-\langle 1346\rangle\langle 25\rangle = -\langle 13\rangle\langle 46\rangle\langle 25\rangle - \langle 1346\rangle\langle 25\rangle - \langle 1346\rangle\langle 25\rangle$$
$$-\langle 1256\rangle\langle 34\rangle = -\langle 12\rangle\langle 56\rangle\langle 34\rangle - \langle 1256\rangle\langle 34\rangle - \langle 1256\rangle\langle 34\rangle$$
$$-\langle 1356\rangle\langle 24\rangle = -\langle 13\rangle\langle 56\rangle\langle 24\rangle - \langle 1356\rangle\langle 24\rangle - \langle 1356\rangle\langle 24\rangle$$
$$-\langle 1456\rangle\langle 23\rangle = -\langle 14\rangle\langle 56\rangle\langle 23\rangle - \langle 1456\rangle\langle 23\rangle - \langle 1456\rangle\langle 23\rangle .$$

As far as the sums over the J_k's in the terms on the right hand sides are concerned, $\langle\bullet\bullet\rangle\langle\bullet\bullet\bullet\bullet\rangle$ yields $J_k^2J_\ell J_nJ_\ell J_n$ and $\langle\bullet\bullet\rangle\langle\bullet\bullet\bullet\bullet\rangle$ yields $J_k^2J_\ell J_n^2J_\ell$ and the sum of these is

$$2(J^2-J_3^2)^3-2(J^2)^2+7J^2J_3^2-5(J_3^2)^2. \qquad (27)$$

The sum of the contributions from the $\langle\bullet\bullet\rangle\langle\bullet\bullet\bullet\bullet\rangle$ and $\langle\bullet\bullet\bullet\bullet\rangle\langle\bullet\bullet\rangle$ terms on the right hand sides of (26) is from (11) and (27)

$$-\left(\frac{kT}{I}\right)^3\left\{4e^{-\beta(t_1+t_2-t_3+t_4-t_5-t_6)}+9e^{-\beta(t_1+t_2+t_3-t_4-t_5-t_6)}\right\}\times$$
$$\left\{2(J^2-J_3^2)^3-2(J^2)^2+7J^2J_3^2-5(J_3^2)^2\right\}. \qquad (28)$$

Finally we collect the $\langle\bullet\bullet\rangle\langle\bullet\bullet\rangle\langle\bullet\bullet\rangle$ contributions. These arise from such terms in (10), (23) and (26), and their sum is

$$\langle 13\rangle\langle 25\rangle\langle 46\rangle + \langle 13\rangle\langle 26\rangle\langle 45\rangle + \langle 15\rangle\langle 23\rangle\langle 46\rangle + \langle 16\rangle\langle 23\rangle\langle 45\rangle$$
$$+ 2\langle 14\rangle\langle 25\rangle\langle 36\rangle + 2\langle 14\rangle\langle 26\rangle\langle 35\rangle + 2\langle 15\rangle\langle 24\rangle\langle 36\rangle \qquad (29)$$
$$+ 2\langle 15\rangle\langle 26\rangle\langle 34\rangle + 2\langle 16\rangle\langle 24\rangle\langle 35\rangle + 2\langle 16\rangle\langle 25\rangle\langle 34\rangle .$$

The sum over the J_k's for each term of this is $J_k^2J_\ell^2J_n^2$, that is $(J^2-J_3^2)^3$. The first four terms have time dependence $e^{-\beta(t_1+t_2-t_3+t_4-t_5-t_6)}$ and the rest have time dependence $e^{-\beta(t_1+t_2+t_3-t_4-t_5-t_6)}$. Hence (29) is equal to

$$\left(\frac{kT}{I}\right)^3(J^2-J_3^2)^3\left\{4e^{-\beta(t_1+t_2-t_3+t_4-t_5-t_6)}+12e^{-\beta(t_1+t_2+t_3-t_4-t_5-t_6)}\right\}. \qquad (30)$$

On summing we obtain from (10), (25), (28) and (30) that

$$\Omega^{(6)}(t_1)=-\left(\frac{kT}{I}\right)^3\left\{\left[9(J^2-J_3^2)J_3^2+4J^2-16J_3^2\right]\int_0^{t_1}dt_2\cdots\int_0^{t_5}dt_6\,e^{-\beta(t_1+t_2-t_3+t_4-t_5-t_6)}\right.$$
$$\left.+\left[21(J^2-J_3^2)J_3^2+20J^2-65J_3^2\right]\int_0^{t_1}dt_2\cdots\int_0^{t_5}dt_6\,e^{-\beta(t_1+t_2+t_3-t_4-t_5-t_6)}\right\}. \qquad (31)$$

5. Correlation functions for spherical harmonics

We see from (7), (17), (21) and (31) that

$$
\begin{aligned}
\frac{d\langle R(t_1,0)\rangle}{dt_1} = -\Big[&\frac{kT}{I}(J^2-J_3^2)\int_0^{t_1} e^{-\beta(t_1-t_2)}\,dt_2 \\
&+\left(\frac{kT}{I}\right)^2(2J^2-5J_3^2)\int_0^{t_1} dt_2\int_0^{t_2} dt_3\int_0^{t_3} dt_4\, e^{-\beta(t_1+t_2-t_3-t_4)} \\
&+\left(\frac{kT}{I}\right)^3\Big\{\big[9(J^2-J_3^2)J_3^2+4J^2-16J_3^2\big]\int_0^{t_1} dt_2\cdots\int_0^{t_5} dt_6\, e^{-\beta(t_1+t_2-t_3+t_4-t_5-t_6)} \\
&\qquad+\big[21(J^2-J_3^2)J_3^2+20J^2-68J_3^2\big]\int_0^{t_1} dt_2\cdots\int_0^{t_5} dt_6\, e^{-\beta(t_1+t_2+t_3-t_4-t_5-t_6)}\Big\} \\
&+\cdots\Big]\langle R(t_1,0)\rangle .
\end{aligned}
$$

This can be integrated immediately to give

$$
\begin{aligned}
\langle R(t,0)\rangle = \exp\Big\{-\Big[&\frac{kT}{I}(J^2-J_3^2)\,I_1^{(2)}(t)+\left(\frac{kT}{I}\right)^2(2J^2-5J_3^2)\,I_2^{(4)}(t) \\
&+\left(\frac{kT}{I}\right)^3\Big\{\big[9(J^2-J_3^2)J_3^2+4J^2-16J_3^2\big]I_3^{(6)}(t) \\
&+\big[21(J^2-J_3^2)J_3^2+20J^2-68J_3^2\big]I_4^{(6)}(t)\Big\}+\cdots\Big]\Big\}
\end{aligned}
\qquad (32)
$$

on recalling that R(0,0) is the identity operator. The time dependent terms on the right hand side are defined in equation (62) and Appendix of FLM. Now by definition

$$
\langle D^j_{mm'}(\alpha(t),\beta(t),\gamma(t))\rangle = \int_0^{2\pi} d\alpha(0)\int_0^{\pi}\sin\beta(0)\,d\beta(0)\,Y^*_{jm}(\beta(0),\alpha(0))\langle R(t,0)\rangle Y_{jm'}(\beta(0),\alpha(0)). \qquad (33)
$$

In substituting for $\langle R(t,o)\rangle$ from (32) we remark that, since J_3 commutes with J_x, J_y, J_z [cf. Brink and Satchler 1975 p. 26],

$$
J_3^2\, Y_{jm'}(\beta(0),\alpha(0)) = R(t,0)^{-1} J_3^2\, Y_{jm'}(\beta(t),\alpha(t)) = 0,
$$

because in the present model the third component of angular velocity vanishes. We may therefore replace every J_3^2 by zero and every J^2 by j(j + 1) times the unit matrix in 2j + 1 dimensions. Thus

$$
\langle D^j_{mm'}(\alpha(t),\beta(t),\gamma(t))\rangle = \delta_{mm'}\exp\Big\{-j(j+1)\Big[\frac{kT}{I}I_1^{(2)}(t)+\left(\frac{kT}{I}\right)^2 2I_2^{(4)}(t)+\left(\frac{kT}{I}\right)^3\big(4I_3^{(6)}(t)+20I_4^{(6)}(t)\big)+\cdots\Big]\Big\},
$$

where we have employed the orthonormality property of the Y_{js}. On the other hand the stochastic averaging process denoted by <•••> is independent of the configuration space variables, and so we have from (33)

$$
\begin{aligned}
\langle D^j_{mm'}(\alpha(t),\beta(t),\gamma(t))\rangle &= \int_0^{2\pi} d\alpha(0)\int_0^{\pi}\sin\beta(0)\,d\beta(0)\,\langle Y^*_{jm}(\beta(0),\alpha(0))R(t,0)Y_{jm'}(\beta(0),\alpha(0))\rangle \\
&= \int_0^{2\pi} d\alpha(0)\int_0^{\pi}\sin\beta(0)\,d\beta(0)\,\langle Y^*_{jm}(\beta(0),\alpha(0))Y_{jm'}(\beta(t),\alpha(t))\rangle \\
&= \int_0^{2\pi} d\alpha(0)\int_0^{\pi}\sin\beta(0)\,d\beta(0)\,\langle Y^*_{jm'}(\beta(t),\alpha(t))Y_{jm}(\beta(0),\alpha(0))\rangle
\end{aligned}
$$

since $\langle D^j_{mm'}(\alpha(t),\beta(t),\gamma(t))\rangle$ is real. The last integral combines the stochastic averaging process with an averaging over the initial configuration, and may properly be called the correlation function of the spherical harmonics $Y_{jm'}$ and Y_{jm}. This vanishes for m' ≠ m, and for m' = m it is equal to the exponential in (34).

For applications to the theory of dielectric relaxation we put j = 1, m = m' = 0 in (34) and using (5) obtain

$$
\langle\cos\beta(t)\rangle = \exp\Big\{-2\frac{kT}{I}I_1^{(2)}(t) - 4\left(\frac{kT}{I}\right)^2 I_2^{(4)}(t) - \left(\frac{kT}{I}\right)^3\big[8I_3^{(6)}(t)+40I_4^{(6)}(t)\big]-\cdots\Big\},
$$

where $\beta(t)$ is the angle between the orientation of the dipole axis at time t and time zero. On expanding the last exponential and employing eq. (A.5) of FLM we find that

$$
\begin{aligned}
\langle\cos\beta(t)\rangle = 1 &- \frac{2kT}{I}I_1^{(2)}(t) + 4\left(\frac{kT}{I}\right)^2\big[I_1^{(4)}(t)+I_2^{(4)}(t)\big] \\
&- \left(\frac{kT}{I}\right)^3\big[8I_1^{(6)}(t)+16I_2^{(6)}(t)+8I_3^{(6)}(t)+16I_4^{(6)}(t)\big]+\cdots
\end{aligned}
$$

We make a Laplace transform of this equation referring again to the Appendix of FLM:

$$\int_0^\infty \langle \cos\beta(t)\rangle e^{-st}\,dt = \frac{1}{s} - \frac{kT}{I}\frac{2}{s^2(s+\beta)} + \left(\frac{kT}{I}\right)^2\left[\frac{4}{s^3(s+\beta)^2} + \frac{4}{s^2(s+\beta)^2(s+2\beta)}\right]$$
$$-\left(\frac{kT}{I}\right)^3\left[\frac{8}{s^4(s+\beta)^3} + \frac{16}{s^3(s+\beta)^3(s+2\beta)} + \frac{8}{s^2(s+\beta)^3(s+2\beta)^2}\right. \qquad (35)$$
$$\left.+\frac{16}{s^2(s+\beta)^2(s+2\beta)^2(s+3\beta)}\right] + \cdots.$$

This may be compared with the result deduced from a Fokker-Planck-Kramers equation by Sack [1957 eq. (2.26)], which is equivalent to

$$1 - i\omega\int_0^\infty \langle \cos\beta(t)\rangle e^{-i\omega t}\,dt = 1 - \frac{i\omega/\beta|}{|i\omega/\beta} + \frac{2kT/I\beta^2|}{|1+i\omega/\beta} + \frac{2kT/I\beta^2|}{|2+i\omega/\beta}$$
$$+\frac{4kT/I\beta^2|}{|3+i\omega/\beta} + \frac{4kT/I\beta^2|}{|4+i\omega/\beta} + \frac{6kT/I\beta^2|}{|5+i\omega/\beta} + \cdots.$$

On expanding the continued fraction as a series in powers of $kT/I\beta^2$ we find agreement with the value of the left hand side deduced from (35) with $s = i\omega$.

For the case of the sphere [cf. FLM eq. (63), (80), (81) and Appendix] eq. (34) becomes

$$\langle D^j_{mm'}\{\alpha(t),\beta(t),\gamma(t)\}\rangle = \delta_{mm'}\exp\Big\{-j(j+1)\Big[\frac{kT}{I}I^{(2)}(t) + \left(\frac{kT}{I}\right)^2 I_2^{(4)}(t)$$
$$+\left(\frac{kT}{I}\right)^3\left[I_3^{(6)}(t) + 4I_4^{(6)}(t)\right]$$
$$+\left(\frac{kT}{I}\right)^4\Big[I_4^{(8)}(t) + 8I_5^{(8)}(t) + (-4j(j+1)+16)\,I_7^{(8)}(t)$$
$$+(-10j(j+1)+38)\,I_8^{(8)}(t)\Big] + \cdots\Big\}.$$

This agrees with the result for the linear molecule as far as terms in the exponent proportional to $kT/I\beta^2$. It would be of interest, though laborious, to extend the calculations for the linear molecule to terms proportional to $(kT/I\beta^2)^4$ and so to see whether the j-dependence of the exponent in (34) will continue to be simply j(j + 1).

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