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An exact treatment for non-linear relaxation processes governed by the rotational Smoluchowski equation

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Abstract. Taking into account a non-linear term in the Smoluchowski equation for the rotational Brownian motion of a symmetrical top, we have obtained exactly the Laplace transform of the conditional probability density function in terms of infinite continued fractions.

1. Introduction

We shall calculate the conditional probability density function $\rho(\theta, t)$ from the rotational Smoluchowski equation for a symmetric top (Morita 1978a):

$$\frac{\partial \rho}{\partial t}=\frac{1}{\sin \theta} \frac{\partial}{\partial \theta}\left[\sin \theta\left(\frac{k_B T}{I\beta} \frac{\partial \rho}{\partial \theta}+\frac{1}{I\beta} \rho \frac{\partial V(\theta, t)}{\partial \theta}\right)\right], \tag{1}$$

where t is the time, k_B is the Boltzmann constant, T is the absolute temperature, $I\beta$ is the friction constant, θ is the angle which the axis of symmetry of the top makes with an arbitrary direction fixed in space, and $V(\theta, t)$ is the potential energy function.

We shall confine ourselves to the case where

$$V=-B \cos \theta, \tag{2}$$

where B is a constant. Examples in which V can be written as (2) are: (i) the rotational motion of the symmetric top under the influence of the gravitational force with $B=MgR$ where M is the mass of the top, g is the gravitational constant and R is the distance between the centre of mass and the origin in space, (ii) the hindered rotation of the symmetric top with the height of the potential energy barrier V_0, viz. $B=V_0$, and (iii) the interaction of a dipole μ with an external electric field F, in which case $B=\mu F$.

Even though (1) is a linear equation in ρ, ρ may be expressed non-linearly with respect to B. We shall take this non-linearity fully into account. Recently Morita (1978b) has obtained exactly the Laplace transform of the electric polarisation following the sudden application of a constant electric field, by means of an infinite continued fraction. We shall follow this method in calculating the Laplace transform of ρ exactly in terms of infinite continued fractions.

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2. Theoretical treatment

On substituting (2) into (1), we immediately find that

$$\frac{\partial \rho}{\partial t}=\frac{D}{\sin\theta}\frac{\partial}{\partial\theta}\left[\sin\theta\left(\frac{\partial\rho}{\partial\theta}+b\sin\theta\rho\right)\right], \tag{3}$$

where

$$D=k_BT/I\beta \quad \text{and} \quad b=B/k_BT. \qquad (4), (5)$$

We express $\rho(x, t)$ where $x=\cos\theta$ in terms of the Legendre polynomials $P_n(x)$, namely,

$$\rho(x,t)=\sum_{n=0}^{\infty}a_n(t)P_n(x), \tag{6}$$

which leads to

$$a_n(t)=\frac{2n+1}{2}\int_{-1}^{1}\rho(x,t)P_n(x)\,\mathrm{d}x. \tag{7}$$

In order to calculate the conditional probability density function $\rho(x, t)$ we have to use the following initial condition:

$$\rho(x,t)=\delta(x-x_0) \qquad \text{at } t=0, \tag{8}$$

where $\delta(x)$ is the Dirac delta function. Thus it follows from (7) that

$$a_n(0)=\frac{2n+1}{2}P_n(x_0). \tag{9}$$

Now, substituting (6) in (3) and using the relations

$$(x^2-1)\mathrm{d}P_n(x)/\mathrm{d}x=nxP_n(x)-nP_{n-1}(x)$$

and

$$(n+1)P_{n+1}(x)-(2n+1)xP_n(x)+nP_{n-1}(x)=0,$$

we deduce that

$$\mathrm{d}a_0/\mathrm{d}t=0 \tag{10}$$

and

$$\mathrm{d}a_n(t)/\mathrm{d}t=-p_na_n(t)-\lambda q_na_{n-1}(t)-\lambda r_na_{n+1}(t) \qquad (n=1,2,3\ldots), \tag{11}$$

where

$$p_n=Dn(n+1), \qquad q_n=\frac{n(n+1)}{2n-1}, \qquad r_n=-\frac{n(n+1)}{2n+3}, \qquad (12), (13), (14)$$

and

$$\lambda=Db. \tag{15}$$

On taking the Laplace transform of both sides of (9) we find that

$$(s+p_n)A_n(s)+\lambda[q_nA_{n-1}(s)+r_nA_{n+1}(s)]=a_n(0) \qquad (n=1,2,3\ldots), \tag{16}$$

where

$$A_n(s)=\int_0^{\infty}a_n(t)\exp(-st)\,\mathrm{d}t. \tag{17}$$

Equation (16) may be written,

$$(\mathbf{L}+\lambda\mathbf{M})\mathbf{A}=\mathbf{a} \tag{18}$$

where

$$\mathbf{L}=\begin{pmatrix} s+p_1 & 0 & 0 & \dots \\ 0 & s+p_2 & 0 & \dots \\ 0 & 0 & s+p_3 & \dots \\ \dots & \dots & \dots & \dots \end{pmatrix}, \tag{19}$$

$$\mathbf{M}=\begin{pmatrix} 0 & r_1 & 0 & 0 & 0 & \dots \\ q_2 & 0 & r_2 & 0 & 0 & \dots \\ 0 & q_3 & 0 & r_3 & 0 & \dots \\ 0 & 0 & q_4 & 0 & q_4 & \dots \\ \dots & \dots & \dots & & \dots & \dots \end{pmatrix}, \tag{20}$$

$$\mathbf{A}=\begin{pmatrix} A_1(s) \\ A_2(s) \\ A_3(s) \\ \vdots \end{pmatrix}, \tag{21}$$

and

$$\mathbf{a}=\begin{pmatrix} a_1(0)-\lambda q_1 A_0(s) \\ a_2(0) \\ a_3(0) \\ \vdots \end{pmatrix}. \tag{22}$$

At this stage, we wish to calculate the inverse matrix

$$\mathbf{W}=(\mathbf{L}+\lambda\mathbf{M})^{-1} \tag{23}$$

where

$$\mathbf{W}=\begin{pmatrix} w_{1,1} & w_{1,2} & \dots & w_{1,n-1} & w_{1,n} & w_{1,n+1} & \dots \\ w_{2,1} & w_{2,2} & \dots & w_{2,n-1} & w_{2,n} & w_{2,n+1} & \dots \\ w_{3,1} & w_{3,2} & \dots & \dots & \dots & \dots & \dots \\ \dots & \dots & \dots & \dots & \dots & \dots & \dots \end{pmatrix}. \tag{24}$$

Although the method to obtain **W** in a power series of λ is given in the Appendix, in this section we shall show how **W** may be calculated exactly in terms of continued fractions.

In view of the fact that the column matrix

$$W_n=\begin{pmatrix} w_{1,n} \\ w_{2,n} \\ w_{3,n} \\ \vdots \\ w_{n,n} \\ w_{n+1,n} \\ \vdots \end{pmatrix} \tag{25}$$

can be obtained from the relation,

$$W_n = \mathbf{W} F_n \tag{26}$$

where

$$F_n = \begin{pmatrix} 0 \\ 0 \\ \vdots \\ 0 \\ 1 \\ 0 \\ \vdots \end{pmatrix} \quad \left.\begin{matrix} \\ \\ \\ \\ \end{matrix}\right] (n-1) \text{ zeros} \tag{27}$$

We find that

$$(\mathbf{L} + \lambda \mathbf{M}) W_n = F_n. \tag{28}$$

Equations (18), (25) and (28) lead to

$$(s + p_1) w_{1,n} + \lambda r_1 w_{2,n} = \delta_{1,n}, \qquad (m = 1) \tag{29}$$

and

$$(s + p_m) w_{m,n} + \lambda (q_m w_{m-1,n} + r_m w_{m+1,n}) = \delta_{m,n} \qquad (m = 2, 3, \ldots) \tag{30}$$

where $\delta_{m,n}$ is the Kronecker delta. These difference equations may be solved for $w_{m,n}$ by means of continued fractions, namely

$$w_{m,n} = Y_m w_{m+1,n} = Y_m Y_{m+1} \ldots Y_{n-1} w_{n,n} \qquad (m < n) \tag{31}$$

$$w_{m,n} = Z_m w_{m-1,n} = Z_m Z_{m-1} \ldots Z_{n+1} w_{n,n}, \qquad (m > n) \tag{32}$$

and

$$w_{n,n} = (s + p_n + \lambda q_n Y_{n-1} + \lambda r_n Z_{n+1})^{-1} \tag{33}$$

where

$$Y_0 \equiv 0$$

$$Y_m = \cfrac{-\lambda r_m}{s + p_m - \cfrac{\lambda^2 r_{m-1} q_m}{s + p_{m-1} - \cfrac{\lambda^2 r_{m-2} q_{m-1}}{s + p_{n-2} - \ddots - \cfrac{\lambda^2 r_2 q_3}{s + p_2 - \cfrac{\lambda^2 r_1 q_2}{s + p_1}}}}}$$

and

$$Z_m = \cfrac{-\lambda q_m}{s + p_m - \cfrac{\lambda^2 r_m q_{m+1}}{s + p_{m+1} - \cfrac{\lambda^2 r_{m+1} q_{m+2}}{s + p_{m+2} - \ddots}}}.$$

Thus we have calculated $w_{m,n}(s)$ in (24) from which $A_n(s)$ can be obtained. Then on inverting $A_n(s)$, we find $a_n(t)$ from which $\rho(x, t)$ can be determined in view of (6).

3. Discussion

We shall first show that $\rho(x, t)$ satisfies the condition

$$\lim_{t\to\infty} \rho(x, t) = \frac{a_0 b}{\sinh b} \exp(bx). \tag{36}$$

Alternatively, in view of (7) we wish to show

$$a_n(\infty) \equiv \lim_{t\to\infty} a_n(t) = \frac{2n+1}{2} \frac{a_0 b}{\sinh b} \int_{-1}^{1} P_n(x) \exp(bx)\, \mathrm{d}x$$

$$= \frac{2n+1}{2} \frac{a_0 b}{\sinh b} \left(\frac{2\pi}{b}\right)^{1/2} I_{n+1/2}(b) \tag{37}$$

where $I_{n+1/2}(b)$ stands for the modified Bessel function of the first kind of order $n + 1/2$. Equation (37) also can be written (Watson 1944)

$$a_n(\infty) = \frac{2n+1}{2} \frac{a_0}{\sinh b} \left(\exp(b) \sum_{r=0}^{n} \frac{(-1)^r (n+r)!}{r!(n-r)!(2b)^r} \right.$$

$$\left. + (-1)^{n+1} \exp(-b) \sum_{r=0}^{n} \frac{(n+r)!}{r!(n-r)!(2b)^r} \right). \tag{38}$$

This immediately gives

$$a_1(\infty) = 3a_0 L(b) \tag{39}$$

$$a_2(\infty) = 5a_0 \left[1 - \frac{3}{b} L(b) \right] \tag{40}$$

$$\vdots$$

where $L(z)$ represents the Langevin function defined by

$$L(z) = \coth z - 1/z = z[(1/3) - (z^2/45) + (2z^4/945) - \ldots]. \tag{41}$$

In view of the recurrence relation

$$(2n + 1/z) I_{n+1/2}(z) = I_{n-1/2}(z) - I_{n+3/2}(z) \tag{42}$$

we find that

$$\frac{I_{n+1/2}}{I_{n-1/2}} = \cfrac{z}{2n+1+\cfrac{z^2}{2n+3+\cfrac{z^2}{2n+5+\ddots}}}, \qquad (n = 1, 2, 3, \ldots). \tag{43}$$

Therefore it immediately follows from (37) and (43) that

$$\frac{a_n(\infty)}{a_{n-1}(\infty)} = \frac{2n+1}{2n-1} \cfrac{b}{2n+1+\cfrac{b^2}{2n+3+\cfrac{b^2}{2n+5+\ddots}}} \tag{44}$$

Now we shall show that $a_n(\infty)$ in equation (18) in fact satisfies (44). Using (22) together with the theorem concerning the Laplace transform given between (21) and (22) of

Morita (1978b) we find that

$$a_n(\infty) = -\lambda q_1 a_0 \lim_{s\to 0} w_{n,1}. \tag{45}$$

This leads not only to (39) and (40) (see (20) of Morita (1978b)) but also to (44). Thus the condition in (36) has been proved.

At this stage it is worthwhile calculating correlation functions from the present results. On multiplying (18) by $P_m(x_0)$ and averaging over x_0 we obtain

$$\mathscr{L}[\langle P_m(x_0)P_n(x)\rangle] = (2n+1)w_{n,m} \tag{46}$$

where

$$\mathscr{L}[g(t)] = \int_0^\infty g(t)\exp(-st)\,\mathrm{d}t. \tag{47}$$

Particularly when $m = n = 1$ and $m = n = 2$ in (46), we immediately find that

$$\mathscr{L}[\langle\cos\theta(0)\cos\theta(t)\rangle] = (2/3)w_{1,1} = \cfrac{2/3}{s+p_1-\cfrac{\lambda^2 r_1 q_2}{s+p_2-\cfrac{\lambda^2 r_2 q_3}{s+p_3-\cfrac{\lambda^2 r_2 q_4}{s+p_4-\ddots}}}} \tag{48}$$

and

$$\mathscr{L}[\langle P_2(\cos\theta(0))P_2(\cos\theta(t))\rangle] = (2/5)w_{2,2} = \cfrac{2/5}{s+p_2-\cfrac{\lambda^2 r_1 q_2}{s+p_1}-\cfrac{\lambda^2 r_2 q_3}{s+p_3-\cfrac{\lambda^2 r_3 q_4}{s+p_4-\ddots}}}. \tag{49}$$

On expanding $w_{1,1}$ and $w_{2,2}$ in a power series in λ, we find that

$$\mathscr{L}[\langle\cos\theta(0)\cos\theta(t)\rangle] = \frac{2}{3}\left(\frac{1}{s+p_1} + \frac{\lambda^2 r_1 q_2}{(s+p_1)^2(s+p_2)} + \frac{\lambda^4 r_1 r_2 q_2 q_3}{(s+p_1)^2(s+p_2)^2(s+p_3)} + \frac{\lambda^4 r_1^2 q_2^2}{(s+p_1)^3(s+p_2)^2} + \dots\right) \tag{50}$$

and

$$\begin{aligned}\mathscr{L}[\langle P_2(\cos\theta(0))P_2(\cos\theta(t))\rangle] &= \frac{2}{5}\left[\frac{1}{s+p_2} + \frac{\lambda^2}{(s+p_2)^2}\left(\frac{r_1 q_2}{s+p_1} + \frac{r_2 q_3}{s+p_3}\right)\right.\\ &\quad + \lambda^4\left(\frac{r_2^2 q_2^2}{(s+p_1)^2(s+p_2)^3} + \frac{2 r_1 r_2 q_2 q_3}{(s+p_1)(s+p_2)^3(s+p_3)}\right.\\ &\quad \left.\left. + \frac{r_2^2 q_3^2}{(s+p_2)^3(s+p_3)^2} + \frac{r_2 r_3 q_3 q_4}{(s+p_2)^2(s+p_3)^2(s+p_4)}\right) + \dots\right].\end{aligned} \tag{51}$$

These may be inverted, after neglecting higher terms than the order of λ^4, to give

$$\langle\cos\theta(0)\cos\theta(t)\rangle$$
$$=\frac{2}{3}\left(\exp(-p_1t)+\frac{\lambda^2 r_1 q_2}{(p_2-p_1)^2}\{\exp(-p_2t)+[(p_2-p_1)t-1]\exp(-p_1t)\}+\ldots\right) \tag{52}$$

and

$$\langle P_2(\cos\theta(0))P_2(\cos\theta(t))\rangle$$
$$=\frac{2}{5}\left(\exp(-p_2t)+\frac{\lambda^2 r_1 q_2}{(p_1-p_2)^2}\{\exp(-p_1t)+[(p_1-p_2)t-1]\exp(-p_2t)\}\right.$$
$$\left.+\frac{\lambda^2 r_2 q_3}{(p_3-p_2)^2}\{\exp(-p_3t)+[(p_3-p_2)t-1]\exp(-p_2t)\}+\ldots\right). \tag{53}$$

It follows immediately that $\langle\cos\theta(0)\cos\theta(t)\rangle$ and $\langle P_2(\cos\theta(0))P_2(\cos\theta(t))\rangle$ for $\lambda\neq 0$ are not simply exponential decaying functions.

Since we have been unable to find the exact results given in § 2 in the literature, they are useful to check results from a more general formulation concerning non-linear relaxation phenomena than the one treated here as a special case.

Finally it should be noted that the mathematical method used in § 2 can also be applied to find the exact solution of a difference equation in the form of (30).

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Appendix: The calculation of W as a power series in λ

The matrix $\mathbf{W}$ in (23) may be written

$$\mathbf{W}=(\mathbf{L}+\lambda\mathbf{M})^{-1}=[\mathbf{L}(\mathbf{E}+\lambda\mathbf{L}^{-1}\mathbf{M})]^{-1}=(\mathbf{E}+\lambda\mathbf{L}^{-1}\mathbf{M})^{-1}\mathbf{L}^{-1}$$
$$=[\mathbf{E}-\lambda\mathbf{L}^{-1}\mathbf{M}+\lambda^2\mathbf{L}^{-1}\mathbf{M}\mathbf{L}^{-1}\mathbf{M}-\ldots+(-1)^n\lambda^n(\mathbf{L}^{-1}\mathbf{M})^n+\ldots]\mathbf{L}^{-1} \tag{A.1}$$

where the unit matrix $\mathbf{E}$ is defined by

$$\mathbf{E}=\begin{pmatrix}1&0&0&\ldots\\0&1&0&\ldots\\0&0&1&\ldots\\\ldots&\ldots&\ldots&\ldots\end{pmatrix}. \tag{A.2}$$

Since the inverse of the diagonal matrix $\mathbf{L}$ can readily be found, it follows from (A.1) that $\mathbf{W}$ can be calculated simply by obtaining matrix products $(\mathbf{L}^{-1}\mathbf{M})^n\mathbf{L}^{-1}$, which is easy, but becomes tedious as n increases.

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