

THE STOCHASTIC THEORY OF A MOLECULAR REORIENTATION. II. A SIMPLE METHOD FOR DEDUCING AND SOLVING THE ANISOTROPIC ROTATIONAL DIFFUSION EQUATION

BY E. KLUK, K. PASTERNY AND A. CHRZESZCZYK

Institute of Physics, Silesian University, Katowice*

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A Markoff's process uniform on the O_3^+ group is adopted as a model rotational diffusion for rigid molecules in any liquid. Using a theory of representations method, the Kolmogoroff-Planck-Fokker equation (K. P. F.) is obtained. In the next step this equation is reduced to a linear equation system for the correlation functions C_{mn}^l (see text). Assuming uniformity in time, the systems for $l=1,2$ are solved. All previous results appear to be special cases of our theory.

1. Introduction

As this paper is a natural continuation of the former one (Kluk, Chrzesczyk [1]), for compactness and economy we are going to use without any special explanation the symbols from [1]. Now we aim at finding the K. P. F. equation for a Markoff's process uniform on the O_3^+ group. The process introduced above is very often treated as a model of rotational diffusion in liquids (Favro [3], Ivanov [4], Huntress [5]). The general K. P. F. equation in the O_3^+ group should give us, as a special case, the rotational diffusion equation which Favro [3] obtained by the application of a very special method.

2. Deduction of the Kolmogoroff-Planck-Fokker equation on the O_3^+ group

Our method is, in a way, a generalization of the standard method used to obtain the Kolmogoroff equation for $R^{(n)}$ type spaces (see *e. g.* Gnedenko [2], p. 307-310). Hence we assume that:

1) if $\Omega(g_0)$ is an arbitrarily small neighbourhood of g_0 then

$$\lim_{\Delta t \rightarrow 0} \int_{O_3^+/\Omega(g_0)} p(g^{-1}g_0; t, t-\Delta t) dg = 0$$

* Address: Instytut Fizyki, Uniwersytet Śląski, Uniwersytecka 4, 40-007 Katowice, Poland.

2) the expressions

$$A_\alpha(g)p(g; t, t_0)$$

$$A_\alpha(g)A_\beta(g)p(g; t, t_0)$$

exist, where $A_\alpha(g)$ is an infinitesimal operator of the regular representation of the O_3^+ group (see Appendix);

3) the integrals

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{\Omega(g_0)} \zeta_\alpha(g)p(g; t, t - \Delta t)dg = D'_\alpha(t)$$

$$\lim_{\Delta t \rightarrow 0} \frac{1}{\Delta t} \int_{\Omega(g_0)} \zeta_\alpha(g)\zeta_\beta(g)p(g; t, t - \Delta t)dg = D_{\alpha\beta}(t)$$

where ζ_α is the Lie parameter of the O_3^+ group, are limited.

Now one can write the Chapman-Kolmogoroff-Smoluchowski (C. K. S.) equation

$$p(g^{-1}g_0; t, t_0) = \int_{O_3^+} p(g^{-1}g_1; t, t - \Delta t)p(g_1^{-1}g_0; t - \Delta t, t_0) dg_1 \quad (2.1)$$

and the identity:

$$p(g^{-1}g_0; t - \Delta t, t_0) = \int_{O_3^+} p(g^{-1}g_1; t, t - \Delta t)p(g^{-1}g_0; t - \Delta t, t_0)dg_1. \quad (2.2)$$

On the other hand

$$p(g_1^{-1}g_0; t - \Delta t, t_0) = p(g^{-1}g_0; t - \Delta t, t_0) +$$

$$+ \zeta_\alpha(g^{-1}g_1)A_\alpha(g^{-1})p(g^{-1}g_0; t - \Delta t, t_0) +$$

$$+ \zeta_\alpha(g^{-1}g_1)\zeta_\beta(g^{-1}g_1)A_\alpha(g^{-1})A_\beta(g^{-1})p(g^{-1}g_0; t - \Delta t, t_0). \quad (2.3)$$

Subtracting the Eq. (2.2) from the Eq. (2.1) and dividing the result by Δt , exploiting the conditions (1)–(3) and taking the limit $\Delta t \rightarrow 0$ we obtain the K. P. F. equation:

$$\frac{\partial p(g^{-1}g_0; t, t_0)}{\partial t} - D'_\alpha(t)A_\alpha(g^{-1})p(g^{-1}g_0; t, t_0) -$$

$$- D_{\alpha\beta}(t)A_\alpha(g^{-1})A_\beta(g^{-1})p(g^{-1}g_0; t, t_0) = 0. \quad (2.4)$$

The coefficients $D'_\alpha(t)$ and $D_{\alpha\beta}(t)$ from condition (3) represent rotational diffusion coefficients, and if $D'_\alpha(t) \equiv 0$ while $D_{\alpha\beta}(t)$ does not depend on time the equation (2.4) is equivalent to that of Favro [3]. However, as was suggested by Silescu [8] or Ullman [9], $D_{\alpha\beta}(t)$ may be stochastically dependent on time, then the rotational diffusion equation with constant coefficients should not be used. Also, as we suppose, the omission of the $D'_\alpha(t)$ coefficients must be justified. Finally it is worth noticing that the definitions of D'_α

and $D_{\alpha\beta}$ given in condition (3) are equivalent to the definitions of Ivanov (see Part I, Eqs (3.8a) and (3.8b)) if

$$\lim_{\Delta t \rightarrow 0} \frac{p(g, \Delta t)}{\Delta t} = p(g)$$

where $p(g)$ is the probability of reaching the reorientation g from the reorientation e after one jump.

3. Equations for correlation functions

The range of the function $p(g^{-1}g_0; t, t_0)$ is the O_3^+ group, hence it can be presented by the series of generalized spherical harmonics $D_{mn}^l(g^{-1}g_0)$ (see Part I of this paper or the paper of Huntress [5])

$$p(g^{-1}g_0; t, t_0) = \frac{1}{8\pi^2} \sum_{l=0}^{\infty} \sum_{m,n=-l}^l (2l+1) C_{mn}^l(t, t_0) D_{nm}^l(g^{-1}g_0). \quad (3.1)$$

Let us see what is the statistical sense of the coefficients $C_{mn}^l(t, t_0)$. Consider coordinates $f_m^l(g)$ and $f_m^{l'}(g_0)$ of two spherical tensors given in the laboratory frame. The correlation function for these tensors should be defined in the following way:

$$\langle \overline{f_m^l(g) f_m^{l'}(g_0)} \rangle \stackrel{df}{=} \int_{O_3^+} \int_{O_3^+} \overline{f_m^l(g) f_m^{l'}(g_0)} p(g^{-1}g_0; t, t_0) p(g_0) dg dg_0. \quad (3.1')$$

Using (3.1) and the transformation rules for the spherical tensors one can easily obtain

$$\langle \overline{f_m^l(g) f_m^{l'}(g_0)} \rangle = \frac{\delta_{ll'} \delta_{mm'}}{2l+1} \overline{C_{n'n}^l(t, t_0) f_n^l f_{n'}^{l'}} \quad (3.2')$$

where f_n^l and $f_{n'}^{l'}$ are the coordinates of the discussed tensors in the molecular frame. From now on, referring to $C_{nn}^l(t, t_0)$ as the correlation function is fully understandable.

The equation for correlation functions $C_{nn}^l(t, t_0)$ may be found from the K. P. F. equation (2.4) in the following way. First, the infinitesimal operators A_α are replaced by the operators $I_\alpha = iA_\alpha$, then the last operators undergo some transformation Q and new operators I_{-1}, I_0, I_{+1} are created

$$\begin{pmatrix} I_{-1} \\ I_0 \\ I_{+1} \end{pmatrix} = Q \begin{pmatrix} I_1 \\ I_2 \\ I_3 \end{pmatrix} \equiv \begin{pmatrix} -\frac{i}{\sqrt{2}} & -\frac{1}{\sqrt{2}} & 0 \\ 0 & 0 & 1 \\ -\frac{i}{\sqrt{2}} & \frac{1}{\sqrt{2}} & 0 \end{pmatrix} \begin{pmatrix} I_1 \\ I_2 \\ I_3 \end{pmatrix} \quad (3.2)$$

where the Q rows are numbered by $-1, 0, 1$ and Q columns by $1, 2, 3$. Simultaneously the Q transformation acts on the rotational diffusion tensors and the new coordinates of these tensors have the form:

$$D'_m(t) = Q_{m\alpha} D'_\alpha(t) \quad (3.3)$$

$$D_{mn}(t) = Q_{m\alpha} Q_{n\beta} D_{\alpha\beta}(t) \quad (3.4)$$

where $\alpha, \beta = 1, 2, 3$ and $m, n = -1, 0, 1$. Finally, after all these transformations Eq. (2.4) may be written as follows:

$$\left(\frac{\partial}{\partial t} + D'_m(t) I_m + D_{mn}(t) I_m I_n \right) p(g^{-1} g_0; t, t_0) = 0. \quad (3.5)$$

Now, inserting (3.1) into (3.5) and using the properties of I_α operators (see Appendix) together with orthogonality for the $D^l_m(g)$ (Gelfand [6], Vilenkin [10]) we have

$$\begin{aligned} & \frac{\partial C^l_{mn}(t, t_0)}{\partial t} + i D'_p(t) \alpha_{n+p, -p}^l C^l_{m, n+p}(t, t_0) + \\ & + (-1)^{p+q} D_{p,q}(t) \alpha_{n+p+q, -q}^l \alpha_{n+p, -p}^l C^l_{m, n+p+q}(t, t_0) = 0 \end{aligned} \quad (3.6)$$

where

$$\begin{aligned} \alpha_{n, -1}^l &= \frac{1}{\sqrt{2}} \alpha_n^l, & \alpha_{n, 0}^l &= n, & \alpha_{n, 1}^l &= -\frac{1}{\sqrt{2}} \alpha_{n+1}^l, \\ \alpha_n^l &= \sqrt{(l+n)(l-n+1)}. \end{aligned}$$

Consequently the whole problem of solving the rotational diffusion equation (3.5) is reduced to looking for solutions of (3.6).

4. Correlation functions with $l = 1, 2$ in the case of a time uniform process

For the time uniform process the correlation functions $C^l_{mn}(t, t_0)$ depend only on $t - t_0 = \tau$ and the diffusion coefficients are constant as results from the condition (3), given in the second paragraph. The equations (3.6) also become simpler if the molecular frame is chosen as a proper base of the tensor $D_{\alpha\beta}$. Now (3.4) can be replaced by

$$\begin{aligned} D_{\mp 1, \mp 1} &= -\frac{1}{2} (D_x - D_y), & D_{\mp 1, \pm 1} &= -\frac{1}{2} (D_x + D_y), \\ D_{0, 0} &= D_z, & D_{0, \mp 1} &= D_{\mp 1, 0} = 0. \end{aligned}$$

a) The case $l = 1$

After using the assumptions given above together with the additional one that $D'_m = 0$ we find

$$\begin{aligned} & \frac{\partial C^1_{m, 0}}{\partial \tau} + (D_x + D_y) C^1_{m, 0} = 0 \\ & \frac{\partial C^1_{m, \mp 1}}{\partial \tau} + \left[D_z + \frac{1}{2} (D_x + D_y) \right] C^1_{m, \mp 1} + \frac{1}{2} (D_x - D_y) C^1_{m, \pm 1} = 0. \end{aligned} \quad (4.1)$$

The solutions of these equations which also fulfill the initial condition

$$C_{mn}^1(0) = \delta_{mn} \quad (4.1')$$

have the form

$$\begin{aligned} C_{-1,-1}^1 &= C_{1,1}^1 = \frac{1}{2} [e^{-(D_x+D_z)\tau} + e^{-(D_y+D_z)\tau}], \\ C_{-1,1}^1 &= C_{1,-1}^1 = \frac{1}{2} [e^{-(D_x+D_z)\tau} - e^{-(D_y+D_z)\tau}], \\ C_{0,0}^1 &= e^{-(D_x+D_y)\tau}, \\ C_{\mp 1,0}^1 &= C_{0,\mp 1}^1 = 0. \end{aligned} \quad (4.2)$$

These results are similar to those of Favro [3] and Steele [7] ones. Let us discuss a slightly more complicated situation when the term with D'_m in (3.6) is not equal zero, but molecules have C_n with $n \geq 2$ or a higher symmetry. Now $D'_0 \neq 0$, $D'_{\pm 1} = 0$ and the solution of (3.6) differs from (4.2) only by the functions $C_{\mp 1,\mp 1}^1(\tau)$ where $D_x + D_z$ and $D_y + D_z$ should be replaced by

$$[D_z + \frac{1}{2}(D_x + D_y)] + \sqrt{\frac{1}{4}(D_x - D_y)^2 - D_0'^2}$$

and

$$[D_z + \frac{1}{2}(D_x + D_y)] - \sqrt{\frac{1}{4}(D_x - D_y)^2 - D_0'^2}$$

respectively. As a result the function $C_{00}^1(\tau)$ is unchanged and we have the special case of the symmetry rule which has been given in the former part of this paper [1].

b) The case $l = 2$

Maintaining the assumptions of $l = 1$ with $D'_m \equiv 0$ we obtain:

$$\begin{aligned} \frac{\partial C_{m,0}^2}{\partial \tau} + 3(D_x + D_y)C_{m,0}^2 - \frac{\sqrt{6}}{2}(D_x - D_y)(C_{m,-2}^2 + C_{m,2}^2) &= 0 \\ \frac{\partial C_{m,\pm 1}^2}{\partial \tau} + \left[\frac{5}{2}(D_x + D_y) + D_z \right] C_{m,\pm 1}^2 - \frac{3}{2}(D_x - D_y)C_{m,\mp 1}^2 &= 0 \\ \frac{\partial C_{m,\pm 2}^2}{\partial \tau} + (4D_z + D_x + D_y)C_{m,\pm 2}^2 - \frac{\sqrt{6}}{2}(D_x - D_y)C_{m,0}^2 &= 0. \end{aligned} \quad (4.3)$$

The solutions of these equations which also fulfill the initial condition (4.1') can be written as follows:

$$C_{-2,\mp 2}^2 = C_{2,\pm 2}^2 = \frac{1}{8\sqrt{A}} \{ [(3D_z - D_s) + 2\sqrt{A}]e^{k_1\tau} - [(3D_z - D_s) - 2\sqrt{A}]e^{k_2\tau} \pm e^{-a\tau} \},$$

$$C_{\mp 2,0}^2 = C_{0,\mp 2}^2 = \frac{b}{8\sqrt{A}} (e^{k_1\tau} - e^{k_2\tau}),$$

$$C_{0,0}^2 = \frac{-1}{4\sqrt{A}} \{ [(3D_z - D_s) - 2\sqrt{A}]e^{k_1\tau} - [(3D_z - D_s) + 2\sqrt{A}]e^{k_2\tau} \},$$

$$C_{\mp 1,\mp 1}^2 = \frac{1}{2} [e^{-y\tau} + e^{-x\tau}], \quad C_{\mp 1,\pm 1}^2 = \frac{1}{2} [e^{-y\tau} - e^{-x\tau}],$$

where

$$\begin{aligned} a &= 4D_z + D_x + D_y, & x &= 4D_x + D_y + D_z, & y &= 4D_y + D_x + D_z, \\ k_{1,2} &= -2(D_s \pm \sqrt{\Delta}), & D_s &= D_x + D_y + D_z, & b &= -\sqrt{6}(D_x - D_y), \\ \Delta &= D_x^2 + D_y^2 + D_z^2 - D_x D_y - D_x D_z - D_y D_z. \end{aligned}$$

And again, like for $l = 1$, the results given above are equivalent to those of Favro [3]. After applying them to the expressions (I.6.1) and (I.6.2) (see [1]), the relaxation times T_1 and T_2 can be expressed as functions of diffusion coefficients. In the case of extreme narrowing the results of Huntress are obtained.

5. Conclusions

We believe that most important is not the fact that we could find the rotational diffusion equation using a simpler and more compact mathematical method than the one of Favro [3], but that the same method was used for both parts of our paper ([1] and the present one). Now all results known from the stochastic theory of molecular reorientation have been obtained from a common source, namely from the C. K. S. equation. Moreover, we are sure about the possibility of applying the method developed here to more complicated cases, *e. g.*, non-rigid molecules.

APPENDIX

If we use the Gelfand form of the O_3^+ group representations and simultaneously the Euler angles φ_1, ϑ are the spherical coordinates, the infinitesimal operators for regular representation can be written as follows:

$$\begin{aligned} A_1 &= \frac{\cos \varphi_2}{\sin \vartheta} \frac{\partial}{\partial \varphi_1} - \sin \varphi_2 \frac{\partial}{\partial \vartheta} - \operatorname{ctg} \vartheta \cos \varphi_2 \frac{\partial}{\partial \varphi_2} \\ A_2 &= \frac{\sin \varphi_2}{\sin \vartheta} \frac{\partial}{\partial \varphi_1} + \cos \varphi_2 \frac{\partial}{\partial \vartheta} - \operatorname{ctg} \vartheta \sin \varphi_2 \frac{\partial}{\partial \varphi_2} \\ A_3 &= \frac{\partial}{\partial \varphi_2} \end{aligned} \quad (\text{A.1})$$

where φ_2 is the last Euler angle.

These operators after the transformation Q (3.2) give us the operators I_p which fulfill the equations:

$$I_p D_{mn}^l(g) = \alpha_{n,p}^l D_{m,n+p}^l(g). \quad (\text{A.2})$$

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