Theory of Fluorescence Depolarization by Anisotropic Brownian Rotations

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On the basis of a generalized diffusion equation for the rotational motion of an asymmetric rigid rotor a general expression for steady-state fluorescence depolarization has been obtained.

1. Introduction

The recently detected inertial effect on the behaviour of the fluorescence anisotropy $r = \frac{3}{2} J_\parallel / J - \frac{1}{2}$ as a function of the viscosity η of a solvent for prolate luminescent molecule, the transition moment of which lies along its longer axis (see [1, 2] and refs. quoted there), was explained using the non-Markovian generalized diffusion equation [1]. The aim of the present note is to extend the previous results to the case of anisotropic diffusion and to derive the general expression for a steady-state depolarization. The problem is solved by reducing it to the case of Markovian diffusion and use of the final results of Chuang and Eisenthal [3]. It is worthy of mention that the inertial effect upon r was recently considered by Sarshevskii *et al.* [4] who used the diffusion equation with time-dependent diffusion constant. This approximation is however worse in comparison with our approach [2].

The different treatments of the rotational Brownian motion of a nonpsherical body in terms of a Fokker-Planck-Kramers equation or stochastic integrodifferential equation were presented in papers of Ford, Lewis, McConnell, Scaife, and Morita (see [5] and refs. quoted there) together with an application to the theory of dielectric relaxation.

2. Theory

Consider the rotational Brownian motion of a nonspherical body (molecule) assuming that the axes 1, 2, 3 are the main ones of a friction tensor (ξ_{kl}) and an inertial tensor (I_{kl}). By $p(\boldsymbol{\Omega}, t)$ we denote the probability density of a given orientation $\boldsymbol{\Omega}$ of molecule at time t. Applying the method presented in [1] one can derive the following approximative integrodifferential equation (generalized diffusion equation) for the function $p(\boldsymbol{\Omega}, t)$:

$$\frac{\partial}{\partial t} p(\boldsymbol{\Omega}, t) = -\int_0^t \mathscr{H}[\boldsymbol{G}(s)]\, p(\boldsymbol{\Omega}, t-s)\, \mathrm{d}s \tag{1}$$

where the operator $\mathscr{H}[\boldsymbol{D}]$, $\boldsymbol{D} = (D_1, D_2, D_3)$ is defined as

$$\mathscr{H}[\boldsymbol{D}] = \sum_{k=1}^{3} D_k \mathscr{J}_k^2, \tag{2}$$

and $\vec{\mathscr{J}}$ is the quantum mechanical angular momentum operator; $\{D_k\}$ – real numbers (cf. [3]). The functions $G_k(s)$, $k = 1, 2, 3$ are the angular velocity autocorrelation functions

$$G_k(s) = \langle \omega_k(s)\, \omega_k(0) \rangle, \quad s \geqq 0. \tag{3}$$

The fluorescence anisotropy at time t after an instantaneous light pulse of excitation is given by

$$r(t) = \int \mathrm{d}\boldsymbol{\Omega}\, p(\boldsymbol{\Omega}, t)\, R(\boldsymbol{\Omega}), \tag{4}$$

where the functions $p(\boldsymbol{\Omega}, 0)$ and $R(\boldsymbol{\Omega})$ are determined by the orientation of absorption and emission dipoles, respectively [3]. The steady-state fluorescence anisotropy for an exponential decay of fluorescence is expressed as

$$r = \frac{1}{\tau} \int_0^\infty e^{-t/\tau}\, r(t)\, \mathrm{d}t, \tag{5}$$

where τ is a mean fluorescence life time. Therefore introducing the Laplace transformation

$$f(t) \to \hat{f}(\lambda) = \lambda \int_0^\infty e^{-\lambda t} f(t)\, \mathrm{d}t \tag{6}$$

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and using (1)–(4) and properties of transformation (6) we obtain

$$r = \hat r\left(\frac{1}{\tau}\right) = \int \mathrm{d}\boldsymbol{\Omega} \left\{\left[1 + \tau^2 \mathscr{H}\left[\hat{\boldsymbol{G}}\left(\frac{1}{\tau}\right)\right]\right]^{-1} \cdot p(\boldsymbol{\Omega}, \mathrm{o})\right\} R(\boldsymbol{\Omega}) . \qquad (7)$$

One can easily check that the formula (7) may be obtained from the corresponding expression for a Markovian diffusion equation [3]

$$\frac{\partial}{\partial t} p(\boldsymbol{\Omega}, t) = -\mathscr{H}[\boldsymbol{D}]\, p(\boldsymbol{\Omega}, t) \qquad (8)$$

if we replace D_k by $\hat D_k \equiv \tau \hat G_k(1/\tau)$. Hence we may use the results of paper [3] to obtain the following final expression:

$$r = 0{,}3\left(\frac{4 q_1 q_2 \gamma_1 \gamma_2}{1 + 3(\hat D_3 + \hat D)\tau} + \frac{4 q_2 q_3 \gamma_2 \gamma_3}{1 + 3(\hat D_1 + \hat D)\tau} + \frac{4 q_3 q_1 \gamma_3 \gamma_1}{1 + 3(\hat D_2 + \hat D)\tau} + \frac{\beta + \hat\alpha}{1 + (6\hat D + 2\hat\Delta)\tau} + \frac{\beta - \hat\alpha}{1 + (6\hat D - 2\hat\Delta)\tau}\right). \qquad (9)$$

Here

$\boldsymbol{q} = (q_1, q_2, q_3)$ – unit vector of emission dipole,

$\gamma = (\gamma_1, \gamma_2, \gamma_3)$ – unit vector of absorption dipole,

$$\beta = \sum_{k=1}^{3} q_k^2 \gamma_k^2 - \frac{1}{3},$$

$$\hat\alpha = \frac{1}{\hat\Delta} \sum_{k=1}^{3} \hat D_k \left\{(q_k^2 + \gamma_k^2 - 2 q_k^2 \gamma_k^2) + \sum_{l \neq k} q_l^2 \gamma_l^2\right\}$$

$$\hat D = \frac{1}{3} \sum_{k=1}^{3} \hat D_k ,$$

$$\hat\Delta = \left[\sum_{k=1}^{3} \hat D_k^2 - \frac{1}{2} \sum_{k \neq l = 1}^{3} \hat D_k \hat D_l\right]^{1/2} \qquad (10)$$

and

$$\hat D_k = \int_0^\infty e^{-t/\tau} \langle \omega_k(t)\, \omega_k(0) \rangle \,\mathrm{d}t . \qquad (11)$$

In order to calculate $\hat D_k$ one may use the results of [5], which are exact in the case of a symmetrical body and approximative for an asymmetrical one. However, very often it is sufficient to use an exponential approximation for $\langle \omega_k(t)\, \omega_k(0) \rangle$ which may be obtained from the following approximative Langevin equation, which differs from the exact one [5] by terms of order $(\omega_k \omega_l)$:

$$I_k \frac{\mathrm{d}\omega_k}{\mathrm{d}t} = -\xi_k \omega_k + M_k(t) , \quad k = 1, 2, 3 . \qquad (12)$$

Here $\{I_k\}\{\xi_k\}$ are the diagonal elements of the inertial and friction tensor, respectively; $M_k(t)$ = random torque.

Within this approximation we obtain

$$\hat D_k = D_k \frac{1}{1 + 6 A_k D_k \tau},$$

$$D_k = \frac{kT}{\xi_k}, \quad A_k = \frac{I_k}{6 k T \tau^2}. \qquad (13)$$

For a special case, if $I_1 = I_2 = I$, $\xi_1 = \xi_2 = \xi$, and $\boldsymbol{q}$ or γ is parallel to the axis 3 we have the well-known formula [1], [2]

$$r = r_0 \frac{1 + A\tau/\theta}{1 + (1 + A)\tau/\theta},$$

where

$$\theta = \frac{\xi}{6kT}, \quad A = \frac{I}{6kT\tau^2}, \qquad (14)$$

$r_0 = 0{,}6\,(\cos^2\delta - \frac{1}{3})$, δ-angle between $\boldsymbol{q}$ and γ.

3. Example

Consider a simple, but different from (14), example of application of formula (9). We assume a prolate shape of the molecule but with the transition moment (say $\boldsymbol{q}$) perpendicular to the long axis. Moreover we assume for simplicity that

$$\begin{aligned} &I_1 = I_2 = I \gg I_3 \quad \text{and therefore} \quad A_3 = 0 , \\ &D_1 = D_2 = D \leqq D_3 , \\ &q_1 = 1 , \quad q_2 = q_3 = 0 , \quad \gamma_1^2 = \cos^2\delta , \\ &\gamma_2 = 0 , \quad \gamma_3^2 = 1 - \cos^2\delta . \end{aligned} \qquad (15)$$

Usually we assume that $\xi_k \sim \eta$, where η is the macroscopical viscosity of the solution. The experimental results may be represented as the function [1, 2]

$$r_0/r = g\,(1/\eta) . \qquad (16)$$

It is convenient to introduce a new variable θ,

$$\frac{1}{\theta} = \frac{1}{\tau} \left.\frac{\mathrm{d}g(x)}{\mathrm{d}x}\right|_{x=0} \cdot \frac{1}{\eta}, \qquad (17)$$

and to compare the experimental results with theoretical expressions for the function

$$r_0/r = f(\tau/\theta)\,. \tag{18}$$

After long but simple calculations one can obtain, using (9)−(13), the function $f(\cdot)$ for the model described by (15) (τ is assumed to be a constant).

$$y = f(x) = \frac{\{1 + F(x)\,H(x)\}\{1 + F(x)[2 - H(x)]\}}{1 + F(x)\,W(x)}\,. \tag{19}$$

Here

$$y = r_0/r\,, \quad x = \tau/\theta\,,$$

$$W(x) = 1 + \frac{0.2}{r_0}\,\frac{1 - \chi M(x)}{1 + 2\chi M(x)}\,,$$

$$F(x) = \frac{x}{1-\sigma}\left[\frac{1}{1+2\chi} + \frac{2\chi M(x)}{1+2\chi}\right],$$

$$H(x) = \frac{3\chi M(x)}{1 + 2\chi M(x)}\,,$$

$$M(x) = \left[1 + \frac{A}{1-\sigma}\,x\right]^{-1},$$

$$A = \frac{I}{6kT\tau^2}\,, \quad \sigma = \frac{0.2}{r_0}\,\frac{1-\chi}{1+2\chi} < 1\,,$$

$$r_0 = 0.6\,[\cos^2\delta - \tfrac{1}{3}]\,, \quad \chi = D/D_3 \leqq 1\,.$$

Figure 1 shows plots of the function $y = f(x)$ for a few sets of parameters χ, r_0, A.

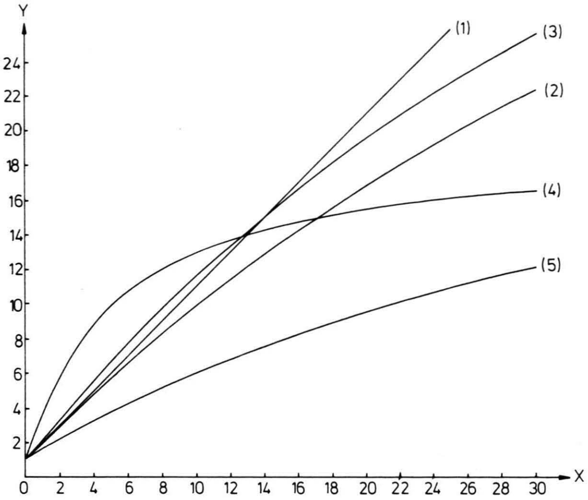

Fig. 1. Function $y = f(x)$.
(1) $\chi = 1$, $A = 0$ (Perrin formula);
(2) $\chi = 0.5$, $r_0 = 0.2$, $A = 0.01$;
(3) $\chi = 0.5$, $r_0 = 0.1$, $A = 0.007$;
(4) $\chi = 0.3$, $r_0 = 0.1$, $A = 0.02$;
(5) $\chi = 0.1$, $r_0 = 0.3$, $A = 0.01$.

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