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 \( r = \frac{1}{2} J_1 / J - \frac{1}{2} \) as a function of the viscosity \( \eta \) 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 nonspherical 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 \((\zeta_{ik})\) and an inertial tensor \((I_{ik})\). By \( p(\Omega, t) \) we denote the probability density of a given orientation \( \Omega \) 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 \( p(\Omega, t) \):

\[
\frac{\partial}{\partial t} p(\Omega, t) = -\int_0^t \mathcal{J}[G(s)] p(\Omega, t-s) \, ds
\]

where the operator \( \mathcal{J}[D] \), \( D = (D_1, D_2, D_3) \) is defined as

\[
\mathcal{J}[D] = \sum_{k=1}^3 D_k \mathcal{J}_k,
\]

and \( \mathcal{J} \) 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

\[
G_k(s) = \langle \omega_k(s) \omega_k(0) \rangle, \quad s \geq 0.
\]

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

\[
r(t) = \int d\Omega p(\Omega, t) R(\Omega),
\]

where the functions \( p(\Omega, 0) \) and \( R(\Omega) \) 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

\[
r = \frac{1}{\tau} \int_0^\infty e^{-r/t} r(t) \, dt,
\]

where \( \tau \) is a mean fluorescence life time. Therefore introducing the Laplace transformation

\[
f(t) \rightarrow \tilde{f}(\lambda) = \lambda \int_0^\infty e^{-\lambda t} f(t) \, dt
\]

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and using (1)-(4) and properties of transformation (6) we obtain
\[ r = \mathcal{R} \left( \frac{1}{\tau} \right) = \int d\Omega \left[ 1 + r^2 \mathcal{R} \left[ G \left( \frac{1}{\tau} \right) \right] \right]^{-1} \cdot p(\Omega, o) R(\Omega). \] (7)

One can easily check that the formula (7) may be obtained from the corresponding expression for a Markovian diffusion equation [3]
\[ p((2, t) = -2f(D)p(\beta, t) \] (8)
if we replace \( D \) by \( D_k = zG_k(\sqrt{z}) \).

Hence we may use the results of paper [3] to obtain the following final expression:
\[ r = 0.3 \left[ \frac{4q_1q_2\gamma_1\gamma_2}{1 + 3(D_3 + D_\perp)\tau} + \frac{4q_2q_3\gamma_2\gamma_3}{1 + 3(D_1 + D_\perp)\tau} \right. \]
\[ + \left. \frac{4q_3q_1\gamma_3\gamma_1}{1 + 3(D_2 + D_\perp)\tau} + \frac{\beta + \hat{\alpha}}{1 + (6\hat{D} + 2\hat{A})\tau} \right] \] (9)

Here
\[ q = (q_1, q_2, q_3) \] — unit vector of emission dipole,
\[ \gamma = (\gamma_1, \gamma_2, \gamma_3) \] — unit vector of absorption dipole,
\[ \beta = \sum_{k=1}^{3} q_k^2 \gamma_k^2 - \frac{1}{3}, \]
\[ \hat{\alpha} = \frac{1}{\mathcal{A}} \sum_{k=1}^{3} \hat{D}_k \left[ (q_k^2 + \gamma_k^2 - 2q_k^2\gamma_k) + \sum_{i \neq k} q_i^2 \gamma_i^2 \right] \]
\[ \hat{D} = \frac{1}{3} \sum_{k=1}^{3} \hat{D}_k, \]
\[ \hat{A} = \left[ \sum_{k=1}^{3} \hat{D}_k^2 - \frac{1}{2} \sum_{k=1}^{3} \hat{D}_k \hat{D}_k \right]^{1/2} \] (10)

and
\[ \hat{D}_k = \int_0^\infty e^{-\xi_k t} \langle \omega_k(t) \omega_k(0) \rangle dt. \] (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 (\( \omega_k \omega_l \)):
\[ I_k \frac{d\omega_k}{dt} = -\xi_k \omega_k + M_k(t), \quad k = 1, 2, 3. \] (12)

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

Within this approximation we obtain
\[ \hat{D}_k = D_k \frac{1}{1 + 6A_k D_k \tau^2}, \]
\[ D_k = \frac{kT}{\xi_k}, \quad A_k = \frac{I_k}{6kT \tau^2}. \] (13)

For a special case, if \( I_1 = I_2 = I, \quad \xi_1 = \xi_2 = \xi, \) and \( q \) or \( \gamma \) is parallel to the axis 3 we have the well-known formula [1], [2]
\[ r = r_0 \frac{1 + A\tau/\theta}{1 + (1 + A)\tau/\theta}, \] (14)
where
\[ \theta = \frac{\xi}{6kT}, \quad A = \frac{I}{6kT \tau^2}, \]
\[ r_0 = 0.6(\cos^2 \delta - \frac{1}{3}), \] \( \delta \)-angle between \( q \) and \( \gamma \).

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 \( q \)) perpendicular to the long axis. Moreover we assume for simplicity that
\[ I_1 = I_2 = I \gg I_3 \] and therefore \( A_3 = 0, \)
\[ D_1 = D_2 = D \equiv D_3, \]
\[ q_1 = 1, \quad q_2 = q_3 = 0, \quad \gamma_1^2 = \cos^2 \delta, \]
\[ \gamma_2^2 = 0, \quad \gamma_3^2 = 1 - \cos^2 \delta. \] (15)

Usually we assume that \( \xi_k \sim \eta \), where \( \eta \) is the macroscopical viscosity of the solution. The experimental results may be represented as the function [1, 2]
\[ \frac{r_0}{r} = g(1/\eta). \] (16)

It is convenient to introduce a new variable \( \theta \),
\[ \frac{1}{\theta} = \frac{1}{\tau} \frac{dg(x)}{dx} \bigg|_{x=0} = \frac{1}{\eta}. \] (17)
and to compare the experimental results with theoretical expressions for the function
\[ r_0/r = f(\tau/\theta). \] (18)

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

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

Here
\[ y = r_0/r, \quad x = \tau/\theta, \]
\[ W(x) = 1 + \frac{0.2}{r_0} \frac{1 - x M(x)}{1 + 2x M(x)}, \]
\[ F(x) = \frac{x}{1 - \sigma} \left[ \frac{1}{1 + 2x} + \frac{2x M(x)}{1 + 2x} \right], \]
\[ H(x) = \frac{3x M(x)}{1 + 2x M(x)}, \]
\[ M(x) = \left[ 1 + \frac{A}{1 - \sigma} x \right]^{-1}, \]
\[ A = \frac{I}{6kT^2}, \quad \sigma = \frac{0.2}{r_0} \frac{1 - x}{1 + 2x} < 1, \]
\[ r_0 = 0.6 [\cos^2 \delta - \frac{1}{3}], \quad \chi = D/D_3 \leq 1. \]

Figure 1 shows plots of the function \( y = \text{f}(x) \) for a few sets of parameters \( \chi, r_0, A \).

Fig. 1. Function \( y = \text{f}(x) \).
(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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