of its derivatives[23–25]. Symmetry coordinates:

$$S_1(A') = 2^{-\frac{1}{2}}(r_1+r_2),$$
$$S_2(A') = t,$$
$$S_3(A') = d,$$
$$S_4(A') = R\,\alpha,$$
$$S_5(A') = (T\,R/2)^{\frac{1}{2}}\,(\beta_{11}+\beta_{12}),$$
$$S_6(A') = (D\,R/2)^{\frac{1}{2}}\,(\beta_{21}+\beta_{22}),$$
$$S_7(A') = s,$$
$$S_8(A') = (S\,T)^{\frac{1}{2}}\,\gamma.$$
$$S_1(A'') = 2^{-\frac{1}{2}}(r_1-r_2),$$
$$S_2(A'') = (T\,R/2)^{\frac{1}{2}}\,(\beta_{11}-\beta_{12}),$$
$$S_3(A'') = (D\,R/2)^{\frac{1}{2}}\,(\beta_{21}-\beta_{22}),$$
$$S_4(A'') = (S\,D)^{\frac{1}{2}}\,\tau.$$

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Time Correlation Functions for Internal and Anisotropic Rotational Motion of Molecules

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By use of Green's functions for the diffusional motion a very concise formulation and computation of correlation functions is possible. For an axially symmetric overall diffusion with internal rotation about one and two axes correlation functions of a second rank spherical tensor are calculated. The results comprise all the solutions of the pertinent problem as given so far and allow the extension of the theory to a wider field of application.

1. Introduction

Nuclear spin relaxation has proved to be a powerful tool for studying molecular motions in liquids. Firstly, valuable information concerning the rotational motions of the molecule to which the nucleus belongs can be obtained. Secondly, internal rotational motions about some fixed molecular axes also have a specific influence on the relaxation behaviour of the nucleus to be considered. This type of rotational motion occurs especially in organic liquids.

The molecular motions enter into the theory of nuclear spin relaxation through the autocorrelation functions. The influence of rotational diffusion on correlation functions has been the subject of several investigations[1–4]. The paper of HUNTRESS[4] treats in detail the case of anisotropic rotational diffusion. However, it is restricted to the case of extreme narrowing and furthermore asymmetry parameters for the various possible interactions are neglected.

The case of internal rotational motions has been studied as well[5–8]. Recently WOESSNER[7] has given a rather general formula for magnetic dipole-dipole relaxation. WALLACH[8] treated internal motion in macromolecules but he did not make allowance for any anisotropic rotations of the macromolecule as a whole. For very long molecules this may be a poor approximation. Furthermore he neglected asymmetry parameters as indicated above.

The author of this article wants to show that by use of Green's functions[9] a very concise formulation of the computation and results is possible. For an overall diffusion of the molecule that is axially symmetric this formulation comprises all the solutions

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of the pertinent problem as given so far and allows the extension of the theory to a wider field of application.

2. Green's Functions and Rotational Transformations

For the one-dimensional rotational diffusion we shall use [9]:

$$g(\chi_0, \chi, t) = (2\,\pi)^{-1} \sum_{J=-\infty}^{+\infty} e^{-iJ(\chi_0-\chi)} \cdot e^{-J^2 D^* t} . \qquad (1)$$

Here, D^* is the diffusion coefficient for the diffusion about the rotational axis, χ_0, χ are the angles of rotation.

For the three-dimensional motion, we shall restrict ourselves to the case of a diffusion tensor with two equal eigenvalues $(D_1 = D_2)$. In this case Green's function [9, 2] may be written in closed form:

$$G(\alpha_0, \beta_0, \gamma_0, \alpha, \beta, \gamma, t) = \sum_{L=0}^{\infty} \sum_{K,M=-L}^{+L} \frac{(2\,L+1)}{8\,\pi^2} D^{(\mathrm{L})*}_{K,M}(\alpha_0, \beta_0, \gamma_0)\, D^{(\mathrm{L})}_{K,M}(\alpha, \beta, \gamma) \cdot e^{-\{D_1 L(L+1) + (D_3 - D_1) K^2\} t} . \qquad (2)$$

D_3 is the diffusion coefficient about, D_1 the diffusion coefficient perpendicular to the axis of symmetry of the diffusion tensor, α_0, β_0, γ_0, α, β, γ are Eulerian angles which describe the orientation of the molecule, $D^{(\mathrm{L})}_{K,M}(\alpha, \beta, \gamma)$ are the elements of the Wigner rotation matrices [10, 11].

Some remarks concerning the Eulerian angles α_0, β_0, γ_0, α, β, γ should be made. Favro [9] has pointed out that the rotations $\Omega_0(\alpha_0, \beta_0, \gamma_0)$ and $\Omega(\alpha, \beta, \gamma)$ are rotations that start from the principle axis system of the diffusion tensor. Thus the rotation can be carried out by three successive steps:

1) rotation of angle α about the molecular fixed z'-axis,
2) rotation of angle β about the nodal line,
3) rotation of angle γ about the laboratory z-axis.

With this transformation $\Omega(\alpha, \beta, \gamma)$ spherical tensors $B^{(\mathrm{L})}_M$ in the laboratory system may be expressed by spherical tensors in the molecular system $B'^{(\mathrm{L})}_M$ [10, 11]:

$$B^{(\mathrm{L})}_M = \sum_{M'=-2}^{+2} D^{(\mathrm{L})}_{M',M}(\alpha, \beta, \gamma)\, B'^{(\mathrm{L})}_{M'} \qquad (3)$$

laboratory system *molecular system*

But there exists another point of view. If now we look at the molecular orientation as described by rotations $\Omega_0'(\alpha_0, \beta_0, \gamma_0)$ and $\Omega'(\alpha, \beta, \gamma)$ which start in the laboratory system, the same physical situation may be described in the molecular system. As seen from the molecular systems these rotations are $\Omega_0(-\gamma_0, -\beta_0, -\alpha_0)$ and $\Omega(-\gamma, -\beta, -\alpha)$. The physical meaning of our Green's function is: If the orientation at zero time was $\Omega_0'[\Omega_0]$ then $G'(\Omega_0', \Omega', t)$ $[G(\Omega_0, \Omega, t)]$ is the probability that the orientation will be $\Omega'[\Omega]$ at time t. Now these probabilities $G'(\Omega_0', \Omega', t)$ as seen from the laboratory system and $G(\Omega_0, \Omega, t)$ as seen from the molecular system must be equal. Thus we get:

$$\begin{aligned} G'(\Omega_0', \Omega', t) &= G(-\gamma_0, -\beta_0, -\alpha_0, -\gamma, -\beta, -\alpha, t) = G(\Omega_0'^{-1}, \Omega'^{-1}, t) \\ &= \sum_{L,K,M} \frac{(2\,L+1)}{8\,\pi^2} \left(D^{(\mathrm{L})*}(\Omega_0')\right)^{-1}_{K,M} \left(D^{(\mathrm{L})*}(\Omega')\right)^{-1}_{K,M} \cdot e^{-\{D_1 L(L+1) + (D_3 - D_1) K^2\} t} \\ &= \sum_{L,K,M} \frac{(2\,L+1)}{8\,\pi^2} (-1)^{M-K} D^{(\mathrm{L})*}_{-M,-K}(\Omega_0') \cdot (-1)^{M-\mathrm{K}} D^{(\mathrm{L})}_{-M,-K}(\Omega') \cdot e^{-\{D_1 L(L+1) + (D_3 - D_1) K^2\} t} \\ &= \sum_{L,K,M} \frac{(2\,L+1)}{8\,\pi^2} D^{(\mathrm{L})*}_{M,K}(\Omega_0') \cdot D^{(\mathrm{L},)}_{M.K}(\Omega') \cdot e^{-\{D_1 L(L+1) + (D_3 - D_1) K^2\} t} . \end{aligned} \qquad (2\,\mathrm{a})$$

We see that the only difference between the Green's function in the laboratory- and the molecular system is the interchange of K and M.

We may also give an equivalent formula for the transformation of spherical tensors like (3), if the rotations are looked at from the laboratory system:

$$\begin{aligned} B^{(\mathrm{L})}_M &= \sum_{M'} D^{(\mathrm{L})}_{M',M}(\Omega)\, B'^{(\mathrm{C})}_{M'} \qquad (3\,\mathrm{a}) \\ &= \sum_{M'} (-1)^{M-M'} D^{(\mathrm{L})}_{-M,-M'}(\Omega')\, B'^{(\mathrm{L})}_{M'} . \end{aligned}$$

Now the calculation of correlation functions may be performed in the molecular system with (2) and (3) or in the laboratory system with (2 a) and (3 a). Because of the more complex structure of (3 a) in this paper it will be carried out in the molecular system. We mention, however, that by use of (2 a) and (3 a) the same results can be obtained.

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3. Calculation of Correlation Functions

When dealing with dipole-dipole interaction one is interested in the corelation functions of the spherical harmonics $y_m^{(2}(\Theta, \Phi)$ (Θ, Φ are spherical coordinates). The more general correlation function of any second rank spherical tensor $B_m^{(2)}$ (for which in short-hand notation we write B^m) will be used in quadrupole — and anisotropic chemical shift relaxation [1].

The correlation functions we want to calculate are of the form:

$$g^{(m)}(t) = \iint \mathrm{d}R_0 \, \mathrm{d}R \, B^{*m}(R) \, B^m(R_0) \cdot p \cdot P(R_0, R, t) . \tag{4}$$

The rotations R_0, R now are taken to describe not only the orientation of the molecule but also the internal degrees of freedom.

If the overall orientation at zero time was R_0 then the probability that the orientation will be R at time t is $P(R_0, R, t)$. p is the a priori probability for any orientation R_0.

Now we shall decompose the orientation R at time t into rotations Ω, Ω' and Ω''. Each of these rotations leads from one coordinate system of physical significance to another.

x, y, z ↑	laboratory system,
$\Omega(\alpha, \beta, \gamma)$	rotation which transforms the principle axis system of the diffusion tensor to the laboratory system,
x', y', z' ↑	principle axes system of the diffusion tensor,
$\Omega'(\alpha', \beta', \gamma')$	rotation which transforms the z'' axis into the z' axis. z'' is the axis for the intramolecular rotation,
x'', y'', z'' ↑	coordinate system which is fixed in the rotating molecular group,
$\Omega''(\alpha'', \beta'', \gamma'')$	rotation which transforms the principle axis system of the second rank spherical tensor under consideration into the system x'', y'', z'',
x_0, y_0, z_0	principle axis sytem of the second rank spherical tensor.

An analogous decomposition of the overall orientation R_0 will be labelled with an index zero. Now the above mentioned transformations will be carried out step by step.

By use of Eq. (3) we can write for $g^{(\mathrm{m})}(t)$ as given by Eq. (4):

$$\begin{aligned} g^{(m)}(t) &= \iint \mathrm{d}R_0 \, \mathrm{d}R \sum_{n=-2}^{+2} D_{n,m}^{(2)}(\Omega_0) \, B'^n \cdot \sum_{l=-2}^{+2} D_{l,m}^{(2)*}(\Omega) \, B'^{l*} \cdot p \cdot P(R_0, R, t) \\ &= \iint \mathrm{d}R_0 \, \mathrm{d}R \sum_{n=-2}^{+2} D_{n,m}^{(2)}(\Omega_0) \sum_{j=-2}^{+2} D_{j,n}^{(2)}(\Omega_0') \, B''^j \sum_{l=-2}^{+2} D_{l,m}^{(2)*}(\Omega) \sum_{k=-2}^{+2} D_{k,l}^{(2)*}(\Omega') \, B''^{k*} \cdot p \cdot P(R_0, R, t) \\ &= \iint \mathrm{d}R_0 \, \mathrm{d}R \sum_{n=-2}^{+2} D_{n,m}^{(2)}(\Omega_0) \sum_{j=-2}^{+2} D_{j,n}^{(2)}(\Omega_0') \sum_{j'=-2}^{+2} D_{j',j}^{(2)}(\Omega_0'') \, B^{0j'} \\ &\quad \cdot \sum_{l=-2}^{+2} D_{l,m}^{(2)*}(\Omega) \sum_{k=-2}^{+2} D_{k,l}^{(2)*}(\Omega') \sum_{k'=-2}^{+2} D_{k',k}^{(2)*}(\Omega'') \, B^{0k'*} \cdot p \cdot P(R_0, R, t) . \end{aligned} \tag{5}$$

Next we must consider the form of the function $P(R_0, R, t)$. The rotational diffusion of the whole molecule is described by the rotations Ω_0, Ω and therefore the Green's function for the three-dimensional motion has to be used. The a priori probability for an orientation Ω_0 is $1/8\pi^2$. The internal rotational motion about the axis z'' is taken to follow the one-dimensional Green's function with the a priori probability $1/2\pi$.

For $p \cdot P(R_0, R, t) \, \mathrm{d}R_0 \, \mathrm{d}R$ in (5) we write, using Eqs. (1) and (2):

$$\begin{aligned} p \cdot P(R_0, R, t) &= \frac{1}{2\pi} g(\chi_0, \chi, t) \frac{1}{8\pi^2} G(\Omega_0, \Omega, t) \, \mathrm{d}\chi_0 \, \mathrm{d}\chi \, \mathrm{d}\Omega_0 \, \mathrm{d}\Omega \\ &= \frac{1}{2\pi} \cdot \frac{1}{2\pi} \cdot \sum_{J=-\infty}^{+\infty} e^{iJ(\chi-\chi_0)} \cdot e^{-J^2 D^* t} \frac{1}{8\pi^2} \sum_{L,K,M} \frac{(2L+1)}{8\pi^2} D_{K,M}^{(\mathrm{L})*}(\Omega_0) \, D_{K,M}^{(\mathrm{L})}(\Omega) \\ &\quad \cdot e^{-\{D_1 L(L+1) + (D_3 - D_1) K^2\} t} . \end{aligned}$$

The angles χ_0, χ which measure the internal rotation are of the form:

$$\chi_0 = \gamma'' + \alpha_0' ; \qquad \chi = \gamma'' + \alpha'$$

The only terms which do not vanish after integration over Ω_0, Ω because of orthogonality relations are those for which: $L = 2$, $M = m$, $K = n = l$.

The integration over χ_0, χ leads to: $J = k = j$.
So we get:

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{n,j,j',k'=-2}^{+2} D^{(2)}_{j',j}(\alpha'', \beta'', 0)\, D^{(2)}_{j,n}(0, \beta', \gamma')\, B^{0j'} \cdot D^{(2)*}_{k',j}(\alpha'', \beta'', 0)\, D^{(2)*}_{j,n}(0, \beta', \gamma')\, B^{0k'*} \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t} \cdot e^{-j^2 D^* t} .$$

In this expression the product $D^{(2)}_{j,n}(0, \beta', \gamma') \cdot D^{(2)*}_{j,n}(0, \beta', \gamma')$ occurs which means that $g^{(m)}(t)$ is independent of γ'. As our final result we write

$$g^{(m)}(t) = \sum_{\substack{n=-2\\ j=-2}}^{\substack{+2\\ +2}} \Big| \sum_{j'=-2}^{+2} D^{(2)}_{j',j}(\alpha'', \beta'', 0)\, D^{(2)}_{j,n}(0, \beta', 0)\, B^{0j'} \Big|^2 \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t} \cdot e^{-j^2 D^* t} . \tag{6}$$

Again we may clarify the meaning of the angles. β' is the angle between the symmetry axis of the diffusion tensor and the internal rotation axis, β'' is the angle between this internal rotation axis and the z^0 axis of the principle axis system of the second rank tensor, α'' finally is the angle about the axis z^0 which is necessary to bring x^0, y^0 in the proper directions relative to the internal rotation axis z''.

A short discussion of the case that the reorientation about the internal axis is not diffusive but stepwise by an angle of $2\pi/3$ will be given in the appendix.

For two and more rotational axes the extension of the above calculation is obvious. We only mention the result for two axes. If the angle between the z' axis of the principle axis system of the diffusion tensor and the first internal rotational axis is called β' and the angle between this first and the second rotational axis is called β'', we get:

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{n,j,j'=-2}^{+2} \Big| \sum_{j''=-2}^{+2} D^{(2)}_{j'',j'}(\alpha''', \beta''', 0)\, D^{(2)}_{j',j}(0, \beta'', 0)\, D^{j(2)}_{j.n}(0, \beta', 0)\, B^{0j''} \Big|^2 \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t} \cdot e^{-j^2 D^{*\prime} t} \cdot e^{-j'^2 D^{*\prime\prime} t} . \tag{6 a}$$

Here, $D^{*\prime}$ and $D^{*\prime\prime}$ are the diffusion coefficients for the first and second internal rotational axis. α''' and β''' again are the angles which transform the principle axis system of the second rank tensor into the proper orientation relative to the last internal rotational axis.

For applications of Eq. (6) it is necessary to consider special forms of the $B^{0j'}$.

4. Dipole-Dipole Relaxation

$$B^{0j'} = y^{(2)}_{j'}(\Theta'', \Phi'') .$$

In the principle axis-system $\Theta'' = 0$, $\Phi'' = 0$ which means:

$$B^{0j'} = \delta_{j',0} \cdot \sqrt{5/4\pi} .$$

Now $g^{(m)}(t)$ is independent of α'' and by the use of the relation [10]

$$D^{(l)}_{0,m}(\alpha, \beta, \gamma) = \sqrt{\frac{4\pi}{2l+1}}\, y^{(l)}_m(\beta, \gamma)$$

we get:

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{n,j=-2}^{+2} \big| y^{(2)}_j(\beta'', 0)\, D^{(2)}_{j,n}(0, \beta', 0) \big|^2 \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t} \cdot e^{-D^* j^2 t} . \tag{7}$$

This result has been derived recently in a different manner [7].

5. Quadrupole Relaxation and Anisotropic Chemical Shift Relaxation

The second rank tensor of interest for quadrupole relaxation is the field gradient tensor [1]:

$$B^{00} = \tfrac{1}{2} q ; \qquad B^{0\pm1} = 0 ; \qquad B^{0\pm2} = \frac{1}{2\sqrt{6}}\, q\, \eta ; \tag{8}$$

$q = V_{z^0 z^0}$ is the field gradient in the z^0 direction,

$\eta = \dfrac{V_{x^0 x^0} - V_{y^0 y^0}}{V_{z^0 z^0}}$ is the asymmetry parameter of the field gradient ($V_{x^0 x^0}$ and $V_{y^0 y^0}$ are the field gradients in the directions x^0 and y^0).

For the anisotropic chemical shift tensor one gets [1]:

$$B^{00} = \tfrac{1}{2} \gamma\, \delta_{z^0} ; \qquad B^{0\pm1} = 0 ; \qquad B^{0\pm2} = \frac{1}{2\sqrt{6}}\, \gamma\, \delta_{z^0}\, \eta ; \tag{9}$$

γ is the gyromagnetic ratio, δ_{z^0} is the chemical shift in the z^0 direction. η is given by $\eta = (\delta_{x^0} - \delta_{y^0}) / \delta_{z^0}$.

Here δ_{x^0} and δ_{y^0} are the chemical shifts in the directions x^0 and y^0 respectively.

It is not necessary to write down formulas for the most general case of Eq. (6) since this is straight forward but rather lengthy. Instead, we shall discuss some cases of special interest. By simplifying assumptions we also shall get results which have been discussed earlier. We give them in the same compact formulation as Eq. (6).

1) A first simplification of Eq. (1) arises if one takes $\eta = 0$. Then $j' = 0$ and the result becomes independent of α''.

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{n,j=-2}^{+2} \left| D^{(2)}_{0,j}(0,\beta'',0)\, D^{(2)}_{j,n}(0,\beta',0)\, B^{00} \right|^2 \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t} \cdot e^{-j^2 D^* t}.$$

Again we may introduce the $y^{(l)}_m$:

$$g^{(m)}(t) = \frac{4\pi}{25} \sum_{n,j=-2}^{+2} \left| y^{(2)}_j(\beta'',0)\, D^{(2)}_{j,n}(0,\beta',0)\, B^{00} \right|^2 \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t} \cdot e^{-j^2 D^* t}. \tag{10}$$

This formula can be used for the calculation of relaxation rates for long molecules with internal motions, when the asymmetry parameter is to be neglected.

If furthermore the overall diffusion is isotropic $(D_3 = D_1)$ the summation over n may be carried out with the result:

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{j=-2}^{+2} \left| D^{(2)}_{0,j}(0,\beta'',0) \right|^2 B^{00\,2} \cdot e^{-6D_1 t} \cdot e^{-j^2 D^* t}. \tag{10 a}$$

Functions like this were derived by WALLACH[8].

We also mention the more general case of isotropic overall diffusion of the molecule $(D_3 = D_1)$ with $\eta \neq 0$. Now in Eq. (6) we may take $\beta' = 0$ and get:

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{j=-2}^{+2} \left| \sum_{j'=-2}^{+2} D^{(2)}_{j',j}(\alpha'',\beta'',0) B^{0j'} \right|^2 \cdot e^{-6D_1 t} \cdot e^{-j^2 D^* t}. \tag{11}$$

2) Eq. (6) must give the results for anisotropic rotational motion if there is no internal motion. In Eq. (6) now $D^* = 0$ and the summation over j may be carried out. The angles β'' and β' must be added. For $\beta'' + \beta'$ we again write β'':

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{n=-2}^{+2} \left| \sum_{j=-2}^{+2} D^{(2)}_{j',n}(\alpha'',\beta'',0)\, B^{0j'} \right|^2 \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t}. \tag{12}$$

This result may be used if one deals with non-vanishing η. But the orientation of the principle axis system of the second rank tensor relative to the diffusion tensor must be known.

The correlation function (12) simplifies further if $\eta = 0$.

By use of: $B^{0j'} = \delta_{0j'} \cdot B^{00}$ one finds for $g^{(m)}(t)$:

$$g^{(m)}(t) = \tfrac{1}{5} \sum_{n=-2}^{+2} \left| D^{(2)}_{0,n}(0,\beta',0)\, B^{00} \right|^2 \cdot e^{-\{6D_1 + (D_3 - D_1) n^2\} t}. \tag{12 a}$$

This formula has been derived earlier by SHIMIZU[3].

As is well known, the relaxation rates $1/T_1$ and $1/T_2$ are certain linear combinations[1] of the Fourier transforms of the corelation functions given here. Thus, because of the rather complicated form of Eqs. (6), (7), (10), (11) and (12) the expressions for $1/T_1$, $1/T_2$ or line width will also be complicated. With the formulation of the correlation functions given here it will be easy to write computer programs for evaluating experimental data.

6. Appendix

Another model for the internal axial motion is the stepwise reorientation through an angle of $2\pi/3$. Each orientation $0, 2\pi/3, 4\pi/3$ has an a priori probability $p = \frac{1}{3}$. We assume that the mean lifetime in each site is τ_r. Then the probability that no rotation has taken place until time t is $(\frac{1}{3} + \frac{2}{3} \exp(-t/\tau_r))$

and the probability that a rotation has taken place to one of the other two orientations is

$$\left(\tfrac{1}{3}-\tfrac{1}{3}\exp(-t/\tau_r)\right).$$

The probability $g(\chi_0, \chi, t)$ may be given in terms of these two expressions.

$$\begin{aligned} g(\chi_0, \chi, t) = {} & (\tfrac{1}{3}+\tfrac{2}{3}e^{-t/\tau_r})\left\{\delta(\chi_0)\,\delta(\chi)+\delta\left(\chi_0-\frac{2\pi}{3}\right)\delta\left(\chi-\frac{2\pi}{3}\right)+\delta\left(\chi_0-\frac{4\pi}{3}\right)\delta\left(\chi-\frac{4\pi}{3}\right)\right\} \\ & +(\tfrac{1}{3}-\tfrac{1}{3}e^{-t/\tau_r})\left\{\delta(\chi_0)\,\delta\left(\chi-\frac{2\pi}{3}\right)+\delta(\chi_0)\,\delta\left(\chi-\frac{4\pi}{3}\right)\right. \\ & \qquad +\delta\left(\chi_0-\frac{2\pi}{3}\right)\delta(\chi)+\delta\left(\chi_0-\frac{2\pi}{3}\right)\delta\left(\chi-\frac{4\pi}{3}\right) \\ & \qquad \left.+\delta\left(\chi_0-\frac{4\pi}{3}\right)\delta(\chi)+\delta\left(\chi_0-\frac{4\pi}{3}\right)\delta\left(\chi-\frac{2\pi}{3}\right)\right\}. \end{aligned}$$

δ is Dirac's delta function.

Now the integration over χ_0, χ which leads to Eq. (6) can be again carried out. Except for the time dependence one gets the same result. The time dependent factor in Eq. (6) becomes:

$$e^{-\{6D_1+(D_3-D_1)n^2\}t}\cdot e^{-t/\tau_j}.$$

Here $1/\tau_j$ is given by:

$$\frac{1}{\tau_j}=\begin{cases} 0 & \text{if } j=0, \\ \dfrac{1}{\tau_r} & \text{if } j=\pm 1 \pm 2. \end{cases}$$

Now there are three corelation times less than in the case of diffusional motion. Equivalent modifications appear in Eq. (6 a).

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