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USING THE SMOLUCHOWSKI EQUATION TO CALCULATIONS OF THE DIPOLAR CORRELATION FUNCTIONS IN SOLID STATE NMR

1. Introduction

The investigations of thermally activated molecular or atom internal motions in solids are important applications of nuclear magnetic resonance (NMR) method. At the present time there are a great number of papers describing the calculations of the different NMR values measured in solids with internal mobility. Experimental NMR values are usually the second moment of NMR line, spin-lattice relaxation rates in the laboratory and rotating frames, the time position and amplitude of the solid echo (see [1–4] and references given therein). All of these values are governed by the dipolar correlation function [5]

$$h(t^{//},t^{/}) = W\sum_{i,j}\overline{a_{ij}(t^{//})a_{ij}(t^{/})}, \tag{1}$$

where

$$W = \frac{3}{4}\gamma^4\hbar^2 I(I+1)\frac{1}{N}, \tag{2}$$

and

$$a_{ij}(t') = R_{ij}^{-3}(t')[1-3\cos^2\theta_{ij}(t')]. \tag{3}$$

In Eq. (1) the upper bar denotes the average of the value $a_{ij}(t'')a_{ij}(t')$ on the random motions of spin-pair $i-j$. In Eq. (2) γ and I are the gyromagnetic ratio and nuclear spin, respectively. In Eq. (3) R_{ij} and θ_{ij} are the spherical coordinates of spin-pair $i-j$ vector $\vec{R}_{ij}$ in the laboratory frame where the vector of the external magnetic field is parallel to z -axis.

In the case of the simple model of the single motion with one correlation time τ_c the dipolar correlation function $h_{ij}(t'',t')$ has the form [4]

$$h(|t|) = \overline{M}_2 + \Delta M_2 \exp\left(-\frac{|t|}{\tau_c}\right), \tag{4}$$

where $t = t'' - t'$.

In Eq. (4)

$$\overline{M}_2 = W\sum_{i,j}(\overline{a}_{ij})^2 \tag{5}$$

is the second moment of motionally narrowed NMR line [5] and

$$\Delta M_2 = M_2 - \overline{M}_2. \tag{6}$$

In Eq. (6)

$$M_2 = W\sum_{i,j} a_{ij}^2 \tag{7}$$

is the second moment of NMR line in rigid lattice [5].

Often in solids the internal mobility of molecular groups is not a single motion with one correlation time τ_c. For example a CH_3 group in $N(CH_3)_3$ unit usually rotates about its threefold axis, while the entire unit rotates about its threefold symmetry axes and these complex motion is not described by single correlation time. For those complex motions, it is often used in literature (see [3] and references given therein) the equation (4) as approximation with a single correlation time which is equal to the sum of the inverse of the correlation times of the constituent motions

$$\tau_c^{-1} = \sum_k \tau_{ck}^{-1}. \tag{8}$$

Here τ_{ck} is the correlation time of the k-th type of internal motion.

However, it has been shown (see [3] and references given therein) that this approximation is not valid for the molecular reorientation into asymmetric two potential wells and three potential ones.

The main purpose of this paper is to derive the general equation for the dipolar correlation function (1), which can be used to analyze various kinds of internal motions, described by two correlation times. Our equation is not restricted to two-site or three site potential wells and it can be applicable not only for the case of molecular group reorientation, but also for the case of atom or molecular diffusion.

2. Theory

In order to calculate the correlation function $h_{ij}(t'',t') = \overline{a_{ij}(t'')a_{ij}(t')}$ we consider the following model of the molecular motion in solids. The two nuclei i and j are the nuclei of given molecular group (for example protons of the CH_3, NH_3 groups). The molecular group undergoes two independent thermally activated jumps among discrete lattice sites $\Omega_{\alpha l}$ ($\alpha = 1, 2, \dots, s$; $l = 1, 2, \dots, n$). Here index α denotes the different positions of molecular group in crystal. Index l denotes the different positions of two nuclei i and j in position α of the molecular group in crystal. We assume that the random process describing the molecular motions in solids is stationary Markov process. For stationary Markov process the correlation function $h_{ij}(t'',t')$ depends only on $|t''-t'|$ and $h_{ij}(t)$ ($t > 0$) can be written as:

$$h_{ij}(t) = \sum_{\alpha,\beta} \sum_{l,m} P(\Omega_{\alpha l}) P(\Omega_{\alpha l}, 0 \mid \Omega_{\beta m}, t) a_{ij}(\Omega_{\alpha l}) a_{ij}(\Omega_{\beta m}). \tag{9}$$

Here $P(\Omega_{\alpha l})$ is the probability that at time $t=0$, the random function $a_{ij}(t)$ is equal to $a_{ij}(\Omega_{\alpha l})$, while $P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)$ is the conditional probability that if at time $t=0$ the random function $a_{ij}(t)$ was equal $a_{ij}(\Omega_{\alpha l})$ then at time t this random function will be equal to $a_{ij}(\Omega_{\beta m})$.

For the random Markov process the conditional probability $P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)$ satisfies the Smoluchowski equation:

$$\frac{\partial}{\partial t}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)=\sum_{\gamma=1}^{s}\sum_{k=1}^{n}P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma k},t)W_{\gamma k\to\beta m}, \tag{10}$$

with the conditions:

$$P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},0)=\delta_{\alpha\beta}\delta_{lm}, \tag{11}$$

$$\sum_{\beta=1}^{s}\sum_{m=1}^{n}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)=1, \tag{12}$$

$$\sum_{\beta=1}^{s}\sum_{m=1}^{n}W_{\alpha l\to\beta m}=0. \tag{13}$$

In Eq. (10) $W_{\gamma k\to\beta m}$ $(k\neq m$ and $\alpha\neq\beta)$ is the rate constants which describe the probability that the random variable $\Omega(t)$ changes from $\Omega_{\gamma k}$ to $\Omega_{\beta m}$ by one jump.

We assume that

$$W_{\alpha l\to\alpha m}=W_1\equiv\frac{1}{n\tau_{c1}},\qquad (l\neq m), \tag{14}$$

$$W_{\alpha l\to\beta l}=W_2\equiv\frac{1}{s\tau_{c2}},\qquad (\alpha\neq\beta). \tag{15}$$

In Eq. (14) τ_{c1} is the correlation time described the intermolecular reorientation of two nuclei i and j in the given position α of molecular group in crystal. This time may be describing for example the reorientation of molecule (CH_3 or

NH_3 groups) around the symmetry axes of molecule. In Eq. (15) τ_{c2} is the correlation time described the reorientation of two nuclei i and j between different positions α of molecular group in crystal. This time may be describing for example the jump of the whole molecule in different site in crystal.

Using Eqs. (14) and (15) we have from Eq. (13)

$$\sum_{\beta=1}^{s}\sum_{m=1}^{n} W_{\alpha l\to\beta m} = W_{\alpha l\to\alpha l} + (n-1)W_1 + (s-1)W_2 = 0. \tag{16}$$

From Eqs. (16) we obtain

$$\begin{aligned} W_{\alpha l\to\alpha l} &= (1-n)W_1 + (1-s)W_2 \\ &\equiv \frac{1-n}{n\tau_{c1}} + \frac{1-s}{s\tau_{c2}}. \end{aligned} \tag{17}$$

Using Eqs. (17), (14) and Eq. (15) we may write Eq. (10) in the form

$$\begin{aligned} &\frac{\partial}{\partial t}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t) = \sum_{k} P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha k},t)\cdot W_{\alpha k\to\alpha l} + \sum_{\gamma\neq\alpha} P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma l},t)W_{\gamma l\to\alpha l} \\ &= \left(\frac{1-n}{n\tau_{c1}} + \frac{1-s}{s\tau_{c2}}\right)P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t) + \frac{1}{n\tau_{c1}}\sum_{k\neq l}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha k},t) + \frac{1}{s\tau_{c2}}\sum_{\gamma\neq\alpha} P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma l},t) \\ &= \left(\frac{1-n}{n\tau_{c1}} + \frac{1-s}{s\tau_{c2}}\right)P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t) + \frac{n-1}{n\tau_{c1}}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t) + \frac{s-1}{s\tau_{c2}}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l}), \end{aligned} \tag{18a}$$

$$\begin{aligned} &\frac{\partial}{\partial t}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t) = \sum_{k} P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha k},t)\cdot W_{\alpha k\to\alpha m} + \sum_{\gamma\neq\alpha} P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma m},t)W_{\gamma m\to\alpha m} \\ &= \left(\frac{1-n}{n\tau_{c1}} + \frac{1-s}{s\tau_{c2}}\right)P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t) + \frac{1}{n\tau_{c1}}\sum_{k\neq m}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha k},t) + \frac{1}{s\tau_{c2}}\sum_{\gamma\neq\alpha} P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma m},t) \\ &= \left(-\frac{1}{n\tau_{c1}} + \frac{1-s}{s\tau_{c2}}\right)P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t) + \frac{1}{n\tau_{c1}}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t) + \frac{s-1}{s\tau_{c2}}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t), \end{aligned} \tag{18b}$$

$$\frac{\partial}{\partial t}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t)=\sum_{k} P(\Omega_{\alpha l},0\,|\,\Omega_{\beta k},t)\cdot W_{\beta k\to\beta l}+\sum_{\gamma\neq\beta} P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma l},t)W_{\gamma l\to\beta l}$$

$$=(\frac{1-n}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}})P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t)+\frac{1}{n\tau_{c1}}\sum_{k\neq l}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta k},t)+\frac{1}{s\tau_{c2}}\sum_{\gamma\neq\beta}P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma l},t) \quad (18c)$$

$$=(\frac{1-n}{n\tau_{c1}}-\frac{1}{s\tau_{c2}})P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t)+\frac{n-1}{n\tau_{c1}}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)+\frac{1}{s\tau_{c2}}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t),$$

$$\frac{\partial}{\partial t}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)=\sum_{k} P(\Omega_{\alpha l},0\,|\,\Omega_{\beta k},t)\cdot W_{\beta k\to\beta m}+\sum_{\gamma\neq\beta} P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma m},t)W_{\gamma m\to\beta m}$$

$$=(\frac{1-n}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}})P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)+\frac{1}{n\tau_{c1}}\sum_{k\neq m}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta k},t)+\frac{1}{s\tau_{c2}}\sum_{\gamma\neq\beta}P(\Omega_{\alpha l},0\,|\,\Omega_{\gamma m},t) \quad (18d)$$

$$=(-\frac{1}{n\tau_{c1}}-\frac{1}{s\tau_{c2}})P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)+\frac{1}{n\tau_{c1}}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t)+\frac{1}{s\tau_{c2}}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t),$$

Introducing the notations

$$x(t)\equiv P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t),\qquad \alpha\neq\beta,\ \ l\neq m, \quad (19a)$$

$$y(t)\equiv P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t),\qquad \alpha\neq\beta, \quad (19b)$$

$$z(t)\equiv P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t),\qquad l\neq m, \quad (19c)$$

$$w(t)\equiv P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t), \quad (19d)$$

we may written the system of equations (18) in the form

$$\frac{\partial x(t)}{\partial t}=(-\frac{1}{n\tau_{c1}}-\frac{1}{s\tau_{c2}})\cdot x(t)+\frac{1}{n\tau_{c1}}\cdot y(t)+\frac{1}{s\tau_{c2}}\cdot z(t), \quad (20a)$$

$$\frac{\partial y(t)}{\partial t}=\frac{n-1}{n\tau_{c1}}\cdot x(t)+(\frac{1-n}{n\tau_{c1}}-\frac{1}{s\tau_{c2}})\cdot y(t)+\frac{1}{s\tau_{c2}}\cdot w(t), \quad (20b)$$

$$\frac{\partial z(t)}{\partial t}=\frac{s-1}{s\tau_{c2}}\cdot x(t)+(-\frac{1}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}})\cdot z(t)+\frac{1}{n\tau_{c1}}\cdot w(t), \quad (20c)$$

$$\frac{\partial w(t)}{\partial t}=\frac{s-1}{s\tau_{c2}}\cdot y(t)+\frac{n-1}{n\tau_{c1}}\cdot z(t)+(\frac{1-n}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}})\cdot w(t). \quad (20d)$$

The characteristic determinant of these equations system is

$$
\begin{vmatrix}
-\frac{1}{n\tau_{c1}}-\frac{1}{s\tau_{c2}}-\lambda & \frac{1}{n\tau_{c1}} & \frac{1}{s\tau_{c2}} & 0 \\
\frac{n-1}{n\tau_{c1}} & \frac{1-n}{n\tau_{c1}}-\frac{1}{s\tau_{c2}}-\lambda & 0 & \frac{1}{s\tau_{c2}} \\
\frac{s-1}{s\tau_{c2}} & 0 & -\frac{1}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}}-\lambda & \frac{1}{n\tau_{c1}} \\
0 & \frac{s-1}{s\tau_{c2}} & \frac{n-1}{n\tau_{c1}} & \frac{1-n}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}}-\lambda
\end{vmatrix}
$$

$$
= (\lambda)\cdot(-\frac{1}{\tau_{c1}}-\lambda)\cdot(-\frac{1}{\tau_{c2}}-\lambda)\cdot(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}}+\lambda) = 0. \qquad (21)
$$

From Eq. (21) we have

$$
\lambda_1 = 0, \quad \lambda_2 = -\frac{1}{\tau_{c1}}, \quad \lambda_3 = -\frac{1}{\tau_{c2}}, \quad \lambda_4 = -\frac{1}{\tau_{c1}}-\frac{1}{\tau_{c2}}. \qquad (22)
$$

The solution of system equation (20) has so the form

$$
x(t) = C_{1x} + C_{2x}\exp(-\frac{t}{\tau_{c1}}) + C_{3x}\exp(-\frac{t}{\tau_{c2}}) + C_{4x}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t], \qquad (23a)
$$

$$
y(t) = C_{1y} + C_{2y}\exp(-\frac{t}{\tau_{c1}}) + C_{3y}\exp(-\frac{t}{\tau_{c2}}) + C_{4y}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t], \qquad (23b)
$$

$$
z(t) = C_{1z} + C_{2z}\exp(-\frac{t}{\tau_{c1}}) + C_{3z}\exp(-\frac{t}{\tau_{c2}}) + C_{4z}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t], \qquad (23c)
$$

$$
w(t) = C_{1w} + C_{2w}\exp(-\frac{t}{\tau_{c1}}) + C_{3w}\exp(-\frac{t}{\tau_{c2}}) + C_{4w}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]. \qquad (23d)
$$

The coefficients C_{px}, C_{py}, C_{pz}, C_{pw} $(p = 1, 2, 3, 4)$ we should be determined from the system of equations

$$(-\frac{1}{n\tau_{c1}}-\frac{1}{s\tau_{c2}}-\lambda_p)\cdot C_{px}+\frac{1}{n\tau_{c1}}\cdot C_{py}+\frac{1}{s\tau_{c2}}\cdot C_{pz}=0, \tag{24a}$$

$$\frac{n-1}{n\tau_{c1}}\cdot C_{px}+(\frac{1-n}{n\tau_{c1}}-\frac{1}{s\tau_{c2}}-\lambda_p)\cdot C_{py}+\frac{1}{s\tau_{c2}}\cdot C_{pw}=0, \tag{24b}$$

$$\frac{s-1}{s\tau_{c2}}\cdot C_{px}+(-\frac{1}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}}-\lambda_p)\cdot C_{pz}+\frac{1}{n\tau_{c1}}\cdot C_{pw}=0, \tag{24c}$$

$$\frac{s-1}{s\tau_{c2}}\cdot C_{py}+\frac{n-1}{n\tau_{c1}}\cdot C_{pz}+(\frac{1-n}{n\tau_{c1}}+\frac{1-s}{s\tau_{c2}}-\lambda_p)\cdot C_{pw}=0. \tag{24d}$$

Denoting

$$a=\frac{n\tau_{c1}}{s\tau_{c2}}, \tag{25a}$$

and

$$D_{ps}=\frac{C_{ps}}{C_{px}}, \tag{25b}$$

we write the system of Eqs. (24) in the form

$$(-1-a-\lambda_p^{\prime})+D_{py}+a\cdot D_{pz}=0, \tag{26a}$$

$$(n-1)\cdot a+(1-n-a-\lambda_p^{\prime})\cdot D_{py}+a\cdot D_{pw}=0, \tag{26b}$$

$$(s-1)\cdot a+[-1+(1-s)\cdot a-\lambda_p^{\prime}]\cdot D_{pz}+D_{pw}=0, \tag{26c}$$

$$(s-1)\cdot a\cdot D_{py}+(n-1)\cdot D_{pz}+[(1-n)+(1-s)\cdot a-\lambda_p^{\prime})]\cdot D_{pw}=0, \tag{26d}$$

where

$$\lambda_p^{\prime}=n\tau_{c1}\cdot\lambda. \tag{27}$$

The solution the system of equations (26) has the form

$$D_{py}=(1+a+\lambda_p^{\prime})-a\cdot D_{pz}, \tag{28a}$$

$$D_{pw} = a(1-s) + [1 + (s-1)\cdot a + \lambda_p^{/}]\cdot D_{pz}, \tag{28b}$$

$$D_{pz} = \frac{a\cdot(s-1)\cdot(2\lambda_p^{/} + as + n)}{\lambda_p^{/2} + n\cdot\lambda_p^{/} + a\cdot(s-1)\cdot(2\lambda_p^{/} + as + n)}. \tag{28c}$$

Using Eqs. (22), we have from Eqs. (28)

$$\lambda_1^{/} = 0, \quad D_{1y} = 1, \quad D_{1z} = 1, \quad D_{1w} = 1, \tag{29a}$$

$$\lambda_2^{/} = -n, \quad D_{2y} = 1-n, \quad D_{2z} = 1, \quad D_{2w} = 1-n, \tag{29b}$$

$$\lambda_3^{/} = -sa, \quad D_{3y} = 1, \quad D_{3z} = 1-s, \quad D_{3w} = 1-s, \tag{29c}$$

$$\lambda_4^{/} = -n-sa, \quad D_{4y} = 1-n, \quad D_{4z} = 1-s, \quad D_{4w} = (1-n)(1-s). \tag{29d}$$

Using Eq. (29) we obtain from Eq. (23)

$$\begin{aligned} P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t) \equiv x(t) = C_{1x} + C_{2x}\exp(-\frac{t}{\tau_{c1}}) \\ + C_{3x}\exp(-\frac{t}{\tau_{c2}}) + C_{4x}\exp[-(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}})t], \end{aligned} \tag{30a}$$

$$\begin{aligned} P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t) \equiv y(t) = C_{1x} + C_{2x}(1-n)\exp(-\frac{t}{\tau_{c1}}) \\ + C_{3x}\exp(-\frac{t}{\tau_{c2}}) + C_{4x}(1-n)\exp[-(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}})t], \end{aligned} \tag{30b}$$

$$\begin{aligned} P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t) \equiv z(t) = C_{1x} + C_{2x}\exp(-\frac{t}{\tau_{c1}}) \\ + C_{3x}(1-s)\exp(-\frac{t}{\tau_{c2}}) + C_{4x}(1-s)\exp[-(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}})t], \end{aligned} \tag{30c}$$

$$P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t)\equiv w(t)=C_{1x}+C_{2x}(1-n)\exp(-\frac{t}{\tau_{c1}})$$
$$+C_{3x}(1-s)\exp(-\frac{t}{\tau_{c2}})+C_{4x}(1-n)(1-s)\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]. \quad (30d)$$

Using condition (11) we have from Eq. (30)

$$0=C_{1x}+C_{2x}+C_{3x}+C_{4x}, \quad (31a)$$

$$0=C_{1x}+C_{2x}(1-n)+C_{3x}+C_{4x}(1-n), \quad (31b)$$

$$0=C_{1x}+C_{2x}+C_{3x}(1-s)+C_{4x}(1-s), \quad (31c)$$

$$1=C_{1x}+C_{2x}(1-n)+C_{3x}(1-s)+C_{4x}(1-n)(1-s). \quad (31d)$$

From Eqs. (31) we obtain

$$C_{1x}=-C_{2x}=-C_{3x}=C_{4x}=\frac{1}{ns}. \quad (32)$$

Inserting (32) into Eqs. (30) we have

$$P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)=\frac{1}{ns}-\frac{1}{ns}\exp(-\frac{t}{\tau_{c1}})$$
$$-\frac{1}{ns}\exp(-\frac{t}{\tau_{c2}})+\frac{1}{ns}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t], \quad (33a)$$

$$P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t)=\frac{1}{ns}+\frac{n-1}{ns}\exp(-\frac{t}{\tau_{c1}})$$
$$-\frac{1}{ns}\exp(-\frac{t}{\tau_{c2}})-\frac{n-1}{ns}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t], \quad (33b)$$

$$P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t)=\frac{1}{ns}-\frac{1}{ns}\exp(-\frac{t}{\tau_{c1}})$$
$$+\frac{s-1}{ns}\exp(-\frac{t}{\tau_{c2}})-\frac{s-1}{ns}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t], \quad (33c)$$

$$P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t)=\frac{1}{ns}+\frac{n-1}{ns}\exp(-\frac{t}{\tau_{c1}})$$
$$+\frac{s-1}{ns}\exp(-\frac{t}{\tau_{c2}})+\frac{(1-n)(1-s)}{ns}\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]. \tag{33d}$$

Inserting Eqs. (33) into Eq. (9) and assuming that $P(\Omega_{\alpha l})=1/ns$ we have

$$h_{ij}(t)=\sum_{\alpha,\beta}\sum_{l,m}P(\Omega_{\alpha l})P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)a_{ij}(\Omega_{\alpha l})a_{ij}(\Omega_{\beta m})$$
$$=\sum_{\alpha\neq\beta}\frac{1}{ns}\sum_{l\neq m}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta m},t)a_{ij}(\Omega_{\alpha l})a_{ij}(\Omega_{\beta m})+\sum_{\alpha\neq\beta}\frac{1}{ns}\sum_{l}P(\Omega_{\alpha l},0\,|\,\Omega_{\beta l},t)a_{ij}(\Omega_{\alpha l})a_{ij}(\Omega_{\beta l})$$
$$+\sum_{\alpha}\frac{1}{ns}\sum_{l\neq m}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha m},t)a_{ij}(\Omega_{\alpha l})a_{ij}(\Omega_{\alpha m})+\sum_{\alpha}\frac{1}{ns}\sum_{l}P(\Omega_{\alpha l},0\,|\,\Omega_{\alpha l},t)a_{ij}^2(\Omega_{\alpha l})$$
$$=[1-\exp(-\frac{t}{\tau_{c1}})-\exp(-\frac{t}{\tau_{c2}})+\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]]\cdot[\frac{1}{s}\sum_{\alpha}[\frac{1}{n}\sum_{l}a_{ij}(\Omega_{\alpha l})]]^2$$
$$+[\exp(-\frac{t}{\tau_{c1}})-\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})]]\cdot\frac{1}{n}\sum_{l}[\frac{1}{s}\sum_{\alpha}a_{ij}(\Omega_{\alpha l})]^2$$
$$+[\exp(-\frac{t}{\tau_{c2}})-\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]]\frac{1}{s}\sum_{\alpha}[\frac{1}{n}\sum_{l}a_{ij}(\Omega_{\alpha l})]^2 \tag{34}$$
$$+\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]\frac{1}{s}\sum_{\alpha}\frac{1}{n}\sum_{l}a_{ij}^2(\Omega_{\alpha l}).$$

Using Eqs. (34) we obtain from Eq. (1)

$$h(t)=[1-\exp(-\frac{t}{\tau_{c1}})-\exp(-\frac{t}{\tau_{c2}})+\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]]\cdot W\sum_{i,j}[\frac{1}{s}\sum_{\alpha}[\frac{1}{n}\sum_{l}a_{ij}(\Omega_{\alpha l})]]^2$$
$$+[\exp(-\frac{t}{\tau_{c1}})-\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})]]\cdot\frac{1}{n}W\sum_{i,j}\sum_{l}[\frac{1}{s}\sum_{\alpha}a_{ij}(\Omega_{\alpha l})]^2$$
$$+[\exp(-\frac{t}{\tau_{c2}})-\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]]\frac{1}{s}W\sum_{i,j}\sum_{\alpha}[\frac{1}{n}\sum_{l}a_{ij}(\Omega_{\alpha l})]^2 \tag{35}$$
$$+\exp[-(\frac{1}{\tau_{c1}}+\frac{1}{\tau_{c2}})t]\frac{1}{s}W\sum_{i,j}\sum_{\alpha}\frac{1}{n}\sum_{l}a_{ij}^2(\Omega_{\alpha l}).$$

Because

$$M_2 = W\sum_{i,j} a_{ij}^2(\Omega_{\alpha l}) \tag{36}$$

is the second moment of NMR line in rigid lattice;

$$\overline{M_2} = W\sum_{i,j}[\frac{1}{n}\sum_{l=1}^{n} a_{ij}(\Omega_{\alpha l})]^2 \equiv W\sum_{i,j}\overline{(a_{ij})}^2 \tag{37}$$

is the second moment of motionally narrowed NMR line by the first dynamic process (by the reorientation of molecule around the symmetry axes);

$$\overline{\overline{M_2}} = W\sum_{i,j}[\frac{1}{s}\sum_{\alpha} a_{ij}(\Omega_{\alpha l})]^2 \equiv W\sum_{i,j}\overline{\overline{(a_{ij})}}^2 \tag{38}$$

is the second moment of motionally narrowed NMR line by the second dynamic process (by the “diffusion” of the whole molecule);

$$\langle M_2\rangle = W\sum_{i,j}[\frac{1}{s}\sum_{\alpha}\frac{1}{n}\sum_{l} a_{ij}(\Omega_{\alpha l})]^2 = W\sum_{i,j}\langle a_{ij}\rangle^2 \tag{39}$$

is the second moment of motionally narrowed NMR line by the first and second dynamic processes, the Eq. (35) may be written in the form

$$\begin{aligned} h(t) = &< M_2 > + (\overline{\overline{M_2}} - < M_2 >)\cdot\exp(-\frac{t}{\tau_{c1}}) + (\overline{M_2} - < M_2 >)\cdot\exp(-\frac{t}{\tau_{c2}}) \\ &+ (M_2 + < M_2 > - \overline{M_2} - \overline{\overline{M_2}})\cdot\exp[-(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}})t]. \end{aligned} \tag{40}$$

From Eq. (40) it follows that if we have only one dynamical process ($\tau_{c2} = \infty$), then $\overline{\overline{M_2}} = M_2$, $< M_2 > = \overline{M_2}$ and

$$h(t) = \overline{M_2} + (M_2 - \overline{M_2})\cdot\exp(-\frac{t}{\tau_{c1}}). \tag{41}$$

Obtained Eq. (41) fully coincides with Eq. (4).

From Eq. (40) and Eq. (41) it follows that in the case of complex motions in solids we cannot use the function (41) replacing τ_{c1}^{-1} on $\tau_{c3}^{-1} = \tau_{c1}^{-1} + \tau_{c2}^{-1}$ [3].

The examples of applications of Eq. (40) to calculations of different NMR measurement values will be published in other publications.

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ZASTOSOWANIE RÓWNANIA SMOLUCHOWSKIEGO DO OBLICZENIA DIPOLOWYCH FUNKCJI KORELACJI W MRJ CIAŁ STAŁYCH

Streszczenie

Korzystając z równania Smoluchowskiego wyprowadzono analityczne wyrażenie na dipolową funkcję korelacji dla złożonego ruchu molekularnego zawierającego dwa czasy korelacji.