Calculation of dipolar correlation function in solids with internal mobility

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Abstract

A general equation for the dipolar correlation function, to be used to analyze various kinds of independent internal motions, described by some correlation times τ_{cm} ($m = 1, 2 \ldots k$), has been obtained. The obtained expression has been used to analyze the temperature dependencies of different NMR measured values: second moment: spin–lattice relaxation times; amplitude of solid echoes signals.
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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 [1–15]. All of these values are governed in the polycrystalline sample by the dipolar correlation function [15–17]

$$h(t'', t') = W \sum_{i,j} \overline{a_{ij}(t'')a_{ij}(t')}, \tag{1}$$

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 [9,15]

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

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

In Eq. (4)

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

is the second moment of motionally narrowed NMR line [15] and

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

In Eq. (6)

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

is the second moment of NMR line in rigid lattice [15].

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Often in solids the internal mobility of molecular groups is not a single motion with one correlation time τ_c. For example a NH_4 group in NH_4Cl rotates about its threefold and twofold symmetry axes and these complex motion is not described by single correlation time. For those complex motions, it is often used in literature Eq. (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 (see discussions in Ref. [6])

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

Here τ_{ck} is the correlation time of the kth type of internal motion.

However, it has been shown in [6], that this approximation is not valid for the molecular reorientaions 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 some 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 reorientations, but also for the case of atom or molecular diffusion. It should be note, that in this paper we consider only the classical models of molecular motions. The problem of quantum rotations in NMR was discussed in [18–21].

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 k independent thermally activated motions among discrete lattice sites $\Omega_{s_1 s_2 \ldots s_k} \equiv \Omega_{s_1}\Omega_{s_2}\ldots\Omega_{s_k}$. In each lattice sites defined by indices s_m ($m = 1, 2\ldots k$) the molecular group undergo thermally activated jumps between n_m lattice sites $s_m, s'_m, s''_m \ldots$. As example the possible lattice sites $\Omega_{s_1 s_2} = \Omega_{s_1}\Omega_{s_2}$ of the two nuclei i and j of the molecular group undergoing two independent thermally activated motions are shown in Fig. 1.

The correlation function $h(t'', t')$ can be written as [15]:

$$h(t'', t') = W \sum_{i,j} \sum_{s_1,\ldots,s_k; s'_1,\ldots,s'_k} P[\Omega_{s_1 s_2,\ldots,s_k}(t'')\Omega_{s'_1 s'_2\ldots s'_k}(t')]$$
$$\times a_{ij}(\Omega_{s_1 s_2\ldots s_k})a_{ij}(\Omega_{s'_1 s'_2\ldots s'_k}). \tag{9}$$

Here $P[\Omega_{s_1 s_2\ldots s_k}(t'')\Omega_{s'_1 s'_2\ldots s'_k}(t')]$ is the probability that at time $t = t''$, the random function $a_{ij}(t)$ is equal to $a_{ij}(\Omega_{s_1 s_2\ldots s_k})$ and at time $t = t'$, the random function $a_{ij}(t)$ is equal to $a_{ij}(\Omega_{s'_1 s'_2\ldots s'_k})$. In Eq. (9) indices s_m and s'_m
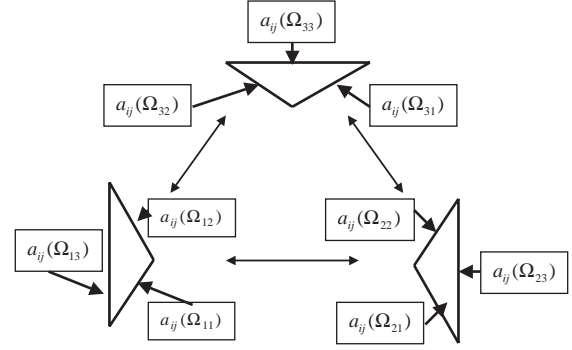

Fig. 1. Schematic representation of the possible lattice sites $\Omega_{s_1 s_2} = \Omega_{s_1}\Omega_{s_2}$ of the two nuclei i and j of the molecular group undergoing two independent thermally activated motions. The first dynamical process is the jumps of the two nuclei i and j of the given molecular group among three lattice sites $\Omega_{s_1 1}$, $\Omega_{s_1 2}$, $\Omega_{s_1 3}$, where index $s_1 = 1, 2, 3$ defines the lattice sites of molecule in lattice; the second dynamical process contains the jumps of whole molecule between three sites of molecule in lattice $\Omega_{1 s_2}$, $\Omega_{2 s_2}$, $\Omega_{3 s_2}$, where index s_2 equals independently to 1, 2, 3.

($m = 1, 2\ldots k$) denote the different lattice sites for the mth thermally activated process.

Because we assume that k thermally activated motions are independent then the probability $P[\Omega_{s_1 s_2\ldots s_k}(t'')\Omega_{s'_1 s'_2\ldots s'_k}(t')]$ can be factorized and we can write Eq. (9) as

$$h(t'', t') = W \sum_{i,j} \sum_{s_1,\ldots,s_k; s'_1,\ldots,s'_k} \prod_{m=1}^{k} P[\Omega_{s_m}(t'')\Omega_{s'_m}(t')]$$
$$\times a_{ij}(\Omega_{s_1 s_2\ldots s_k})a_{ij}(\Omega_{s'_1 s'_2\ldots s'_k}). \tag{10}$$

Here $P[\Omega_{s_m}(t'')\Omega_{s'_m}(t')]$ is the probability that at time $t = t''$, the molecular group occupied the lattice position Ω_{s_m} and at time $t = t''$, this group is in the lattice position $\Omega_{s'_m}$. The probability $P[\Omega_{s_m}(t'')\Omega_{s'_m}(t')]$ describes the mth ($m = 1, 2\ldots k$) thermally activated process from k independent motions.

If we assume that the random process describing the molecular motions in solids is stationary Markov process then for the simple model of the molecular motion between the equivalent potential wells, the probability $P[\Omega_{s_m}(t'')\Omega_{s'_m}(t')]$ is equal [9,10,15]

$$P[\Omega_{s_m}(t'')\Omega_{s'_m}(t')] = \frac{1}{n_m}\left\{\frac{1}{n_m}\left[1 - \exp\left(-\frac{t}{\tau_{cm}}\right)\right]\right.$$
$$\left. + \exp\left(-\frac{t}{\tau_{cm}}\right)\delta_{s_m s'_m}\right\}. \tag{11}$$

Here n_m is the number of lattice sites for the mth thermally activated process. τ_{cm} is the correlation time for this process. In Eq. (11) $t = |t'' - t'|$.

Inserting Eq. (11) into Eq. (10) we obtain the finish result

$$h(t) = \sum_{i,j} \sum_{s_1,\ldots,s_k, s'_1,\ldots,s'_k} \prod_{m=1}^{k} \frac{1}{n_m}\left\{\frac{1}{n_m}\left[1 - \exp\left(-\frac{t}{\tau_{cm}}\right)\right.\right.$$
$$\left.\left. + \exp\left(-\frac{t}{\tau_{cm}}\right)\right]\delta_{s_m s'_m}\right\}a_{ij}(\Omega_{s_1 s_2\ldots s_k})a_{ij}(\Omega_{s'_1 s'_2\ldots s'_k}).$$
$$\tag{12}$$

As example using the obtained Eq. (12) we consider the case of two independent type of molecular motion. In this case from Eq. (12) we have

$$
\begin{aligned}
h(t) &= \Bigg[1 - \exp\left(-\frac{t}{\tau_{c1}}\right) - \exp\left(-\frac{t}{\tau_{c2}}\right) \\
&\quad + \exp\left[-\left(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}}\right)t\right]\Bigg] \\
&\quad \times W \sum_{i,j} \left[\frac{1}{n_2}\sum_{s_2=1}^{n_2}\frac{1}{n_1}\sum_{s_1=1}^{n_1} a_{ij}(\Omega_{s_1 s_2})\right]^2 \\
&\quad + \left[\exp\left(-\frac{t}{\tau_{c1}}\right) - \exp\left[-\left(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}}\right)\right]\right] \\
&\quad \times W \sum_{i,j}\frac{1}{n_1}\sum_{s_1=1}^{n}\left[\frac{1}{n_2}\sum_{s_2=1}^{n_2} a_{ij}(\Omega_{s_1 s_2})\right]^2 \\
&\quad + \left[\exp\left(-\frac{t}{\tau_{c2}}\right) - \exp\left[-\left(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}}\right)t\right]\right] \\
&\quad \times W \sum_{i,j}\frac{1}{n_2}\sum_{s_2=1}^{n_2}\left[\frac{1}{n_1}\sum_{s_1=1}^{n_1} a_{ij}(\Omega_{s_1 s_2})\right]^2 \\
&\quad + \exp\left[-\left(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}}\right)t\right] \\
&\quad \times W \sum_{i,j}\frac{1}{n_2}\sum_{s_2=1}^{n_2}\frac{1}{n_1}\sum_{s_1=1}^{n_1} a_{ij}^2(\Omega_{s_1 s_2}).
\end{aligned}
\tag{13}
$$

It should be note that in Eq. (13) nuclei i and j may be also the nuclei of different mobile molecular group.

If the lattice sites $\Omega_{s_1 s_2}$ are the sites which there are in the rigid lattice, then

$$
M_2 = W \sum_{i,j} a_{ij}^2(\Omega_{s_1 s_2})
\tag{14}
$$

is the second moment of NMR line in rigid lattice;

$$
\overline{M_2} = W \sum_{i,j}\left[\frac{1}{n_1}\sum_{s_1=1}^{n_1} a_{ij}(\Omega_{s_1 s_2})\right]^2 \equiv W \sum_{i,j}\overline{(a_{ij})}^2,
\tag{15}
$$

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

$$
\overline{\overline{M_2}} = W \sum_{i,j}\left[\frac{1}{n_2}\sum_{s_2=1}^{n_2} a_{ij}(\Omega_{s_1 s_2})\right]^2 \equiv W \sum_{i,j}\overline{\overline{(a_{ij})}}^2,
\tag{16}
$$

is the second moment of motionally narrowed NMR line by the second dynamic process (for example, by the "diffusion" of the whole molecule);

$$
\begin{aligned}
\langle M_2 \rangle &= W \sum_{i,j}\left[\frac{1}{n_2}\sum_{s_2=1}^{n_2}\frac{1}{n_1}\sum_{s_1=1}^{n_2} a_{ij}(\Omega_{s_1 s_2})\right]^2 \\
&= W \sum_{i,j}\langle a_{ij}\rangle^2,
\end{aligned}
\tag{17}
$$

is the second moment of motionally narrowed NMR line by the first and second dynamic processes, Eq. (13)

may be written in the form

$$
\begin{aligned}
h(t) &= \langle M_2 \rangle + (\overline{\overline{M_2}} - \langle M_2 \rangle)\exp\left(-\frac{t}{\tau_{c1}}\right) \\
&\quad + (\overline{M_2} - \langle M_2 \rangle)\exp\left(-\frac{t}{\tau_{c2}}\right) \\
&\quad + (M_2 + \langle M_2 \rangle - \overline{M_2} - \overline{\overline{M_2}}) \\
&\quad \times \exp\left[-\left(\frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}}\right)t\right].
\end{aligned}
\tag{18}
$$

From Eq. (18) it follows that if we have only one dynamical process ($\tau_{c2} = \infty$), then $\overline{\overline{M_2}} = M_2$, $\langle M_2 \rangle = \overline{M_2}$ and

$$
h(t) = \overline{M_2} + (M_2 - \overline{M_2})\exp\left(-\frac{t}{\tau_{c1}}\right).
\tag{19}
$$

Obtained Eq. (19) fully coincides with Eq. (4).

From comparison of Eqs. (18) and (19) it follows that in the case of complex motions in solids we cannot use function (19) replacing τ_{c1}^{-1} on $\tau_{c3}^{-1} = \tau_{c1}^{-1} + \tau_{c2}^{-1}$ [6].

Now we consider the examples of applications of Eq. (18) to calculations of different NMR measurement values.

3. The temperature dependence of second moment of NMR line

The temperature dependence of the second moment of NMR line is determined by equation [2,14,15]

$$
M_2(T) = \frac{1}{2\pi}\int_{-\delta\omega}^{\delta\omega} J_0(\omega)\, d\omega.
\tag{20}
$$

In Eq. (20) the function of the spectral density $J_0(\omega)$ is determined by the equation

$$
J_0(\omega) = \int_{-\infty}^{\infty} h(|t|)\exp(i\omega t)\, dt.
\tag{21}
$$

Inserting Eq. (18) into Eq. (21) we have

$$
\begin{aligned}
J_0(\omega) &= \int_{-\infty}^{\infty} h(t)\, dt = \langle M_2\rangle\delta(0) + (\overline{\overline{M_2}} - \langle M_2 \rangle) \\
&\quad \times \frac{2\tau_{c1}}{1 + (\omega\tau_{c1})^2} + (\overline{M_2} - \langle M_2 \rangle) \\
&\quad \times \frac{2\tau_{c2}}{1 + (\omega\tau_{c2})^2} + (M_2 + \langle M_2 \rangle \\
&\quad - \overline{M_2} - \overline{\overline{M_2}})\frac{2\tau_{c3}}{1 + (\omega\tau_{c3})^2},
\end{aligned}
\tag{22}
$$

where

$$
\frac{1}{\tau_{c3}} = \frac{1}{\tau_{c1}} + \frac{1}{\tau_{c2}}.
\tag{23}
$$

Because

$$
\int_{-\beta}^{\beta}\frac{\tau}{1 + (\omega\tau)^2}\, d\omega = 2\tan^{-1}(\beta).
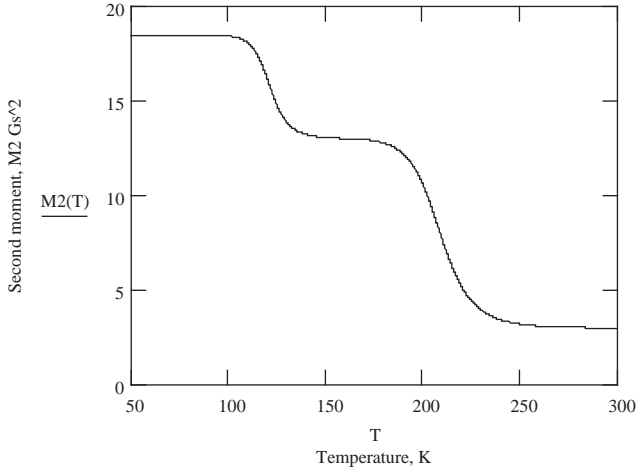\tag{24}
$$

Fig. 2. Temperature dependence of the second moment. The graph represents Eq. (25) for following parameters: $M_2 = 18.47 \times 10^{-8}\,T^2$, $\overline{M_2} = 13 \times 10^{-8}\,T^2$, $\overline{\overline{M_2}} = 0.3 \times M_2 \times 10^{-8}\,T^2$, $\langle M_2 \rangle = 3 \times 10^{-8}\,T^2$; $\tau_{c1} = 10^{-14} \times \exp(20.8\,\text{kJ/mol})\,s$, $\tau_{c2} = 10^{-14} \times \exp(35.8\,\text{kJ/mol})\,s$, $\delta\omega = \sqrt{M_2}$.

inserting Eq. (22) into Eq. (20) we obtain

$$
\begin{aligned}
M_2(T) = &\langle M_2 \rangle + (\overline{\overline{M_2}} - \langle M_2 \rangle)\frac{2}{\pi}\tan^{-1}(\delta\omega\,\tau_{c1}) \\
&+ (\overline{M_2} - \langle M_2 \rangle)\frac{2}{\pi}\tan^{-1}(\delta\omega\,\tau_{c2}) \\
&+ (M_2 + \langle M_2 \rangle - \overline{M_2} \\
&- \overline{\overline{M_2}})\frac{2}{\pi}\tan^{-1}(\delta\omega\,\tau_{c3}).
\end{aligned}
\tag{25}
$$

The temperature dependence of the second moment is shown in Fig. 2.

4. The temperature dependencies of spin–lattice relaxation times

The temperature dependence of the spin–lattice relaxation rates in laboratory T_1^{-1} and rotating $T_{1\rho}^{-1}$ frames in the polycrystalline sample are determined by equations [15–17]

$$
T_1^{-1} = \tfrac{1}{3}[J_0(\omega_0) + 4J_0(2\omega_0)],
\tag{26}
$$

$$
T_{1\rho}^{-1} = \tfrac{1}{6}[3J_0(2\omega_1) + 5J_0(\omega_0) + 2J_0(2\omega_0)].
\tag{27}
$$

In Eqs. (26) and (27) the function of the spectral density $J_0(\omega)$ is determined by Eq. (21).

Inserting Eq. (22) into Eqs. (26) and (27) we have

$$
\begin{aligned}
T_1^{-1} = &\frac{2}{3}(\overline{\overline{M_2}} - \langle M_2 \rangle)\left[\frac{\tau_{c1}}{1 + (\omega_0\tau_{c1})^2} + \frac{4\tau_{c1}}{1 + (2\omega_0\tau_{c1})^2}\right] \\
&+ \frac{2}{3}(\overline{M_2} - \langle M_2 \rangle)\left[\frac{\tau_{c2}}{1 + (\omega_0\tau_{c2})^2} + \frac{4\tau_{c2}}{1 + (2\omega_0\tau_{c2})^2}\right]
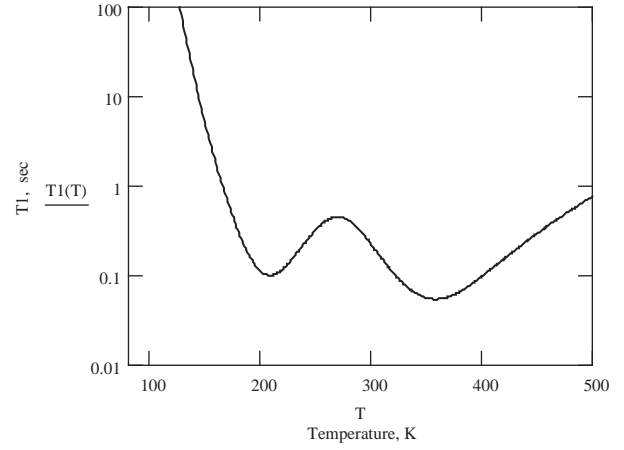\end{aligned}
$$

Fig. 3. Temperature dependencies of T^{-1}. The graph represents Eq. (28) for the same parameters as in Fig. 2; $\omega_0 = 2\pi \times 60 = 376\,\text{MHz rad}$.
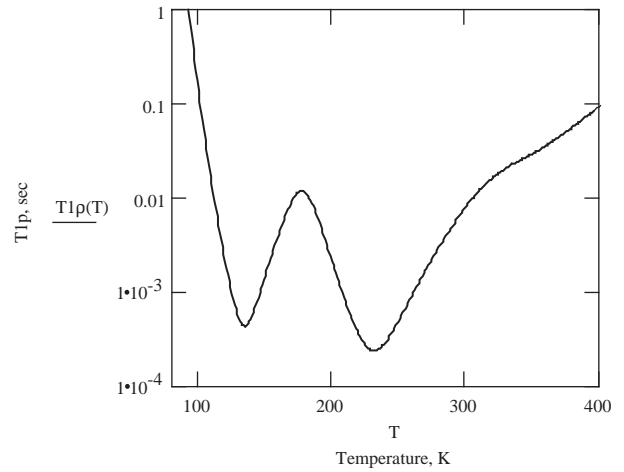

Fig. 4. Temperature dependencies of $T_{1\rho}^{-1}$. The graph represents Eq. (29) for the same parameters as in Figs. 2 and 3; $\omega_0 = 2\pi \times 60 = 376\,\text{MHz rad}$, $\omega_1 = (\pi/2) \times (1/3.6) = 0.43\,\text{MHz rad}$.

$$
\begin{aligned}
&+ \frac{2}{3}(M_2 + \langle M_2 \rangle - \overline{M_2} - \overline{\overline{M_2}}) \\
&\times \left[\frac{\tau_{c3}}{1 + (\omega_0\tau_{c3})^2} + \frac{4\tau_{c3}}{1 + (2\omega_0\tau_{c3})^2}\right],
\end{aligned}
\tag{28}
$$

$$
\begin{aligned}
T_{1\rho}^{-1} = &\frac{1}{3}(\overline{\overline{M_2}} - \langle M_2 \rangle)\left[\frac{3\tau_{c1}}{1 + (2\omega_1\tau_{c1})^2} + \frac{5\tau_{c1}}{1 + (\omega_0\tau_{c1})^2}\right. \\
&\left.+ \frac{2\tau_{c1}}{1 + (2\omega_0\tau_{c1})^2}\right] + \frac{1}{3}(\overline{M_2} - \langle M_2 \rangle) \\
&\times \left[\frac{3\tau_{c2}}{1 + (2\omega_1\tau_{c2})^2} + \frac{5\tau_{c2}}{1 + (\omega_0\tau_{c2})^2} + \frac{2\tau_{c2}}{1 + (2\omega_0\tau_{c2})^2}\right] \\
&+ \frac{1}{3}(M_2 + \langle M_2 \rangle - \overline{M_2} - \overline{\overline{M_2}})\left[\frac{3\tau_{c3}}{1 + (2\omega_1\tau_{c3})^2}\right. \\
&\left.+ \frac{5\tau_{c3}}{1 + (\omega_0\tau_{c3})^2} + \frac{2\tau_{c3}}{1 + (2\omega_0\tau_{c3})^2}\right].
\end{aligned}
\tag{29}
$$

The temperature dependencies of T^{-1} and $T_{1\rho}^{-1}$ are shown in Figs. 3 and 4.

5. The temperature dependence of solid-echo signal

The solid echo signals is determined by equation [9,10].

$$
\begin{aligned}
V(t, t_2, \tau, t_1) = \beta \Bigg[1 - \frac{1}{4} \int_0^{t_1} (t_1 - z)h(z) \Bigg] dz - \frac{1}{2} \int_0^{t_1} zh(z)\, dz \\
- \frac{t_1}{2} \int_{t_1}^{\tau-t_1} h(z)\, dz - \frac{1}{2} \int_{\tau-t_1}^{\tau} (\tau - z)h(z)\, dz \\
- \int_0^{\tau-t_1} [(\tau - t_1) - z]h(z)\, dz \\
- \frac{1}{2} \int_{\tau+t_2-t_1}^{\tau+t_2} [(\tau + t_2 - t_1) - z]\, h(z)\, dz \\
+ \frac{t_1}{2} \int_{\tau+t_2}^{t-t_1} h(z)\, dz + \frac{1}{2} \int_{t-t_1}^{t} (t - z)h(z)\, dz \\
- \int_{t_2}^{\tau+t_2-t_1} (t_2 - z)h(z)\, dz \\
+ (\tau - t_1) \int_{\tau+t_2-t_1}^{t-\tau} h(z)\, dz \\
+ \int_{t-\tau}^{t-t_1} [(t - t_1) - z]h(z)\, dz \\
- \int_0^{t-\tau-t_2} [(t - \tau - t_2) - z]h(z)\, dz + \cdots \Bigg].
\end{aligned}
\tag{30}
$$

Denoting

$$
K_0 = \langle M_2 \rangle,
\tag{31a}
$$

$$
K_1 = \overline{\overline{M_2}} - \langle M_2 \rangle,
\tag{31b}
$$

$$
K_2 = \overline{M_2} - \langle M_2 \rangle,
\tag{31c}
$$

$$
K_3 = M_2 + \langle M_2 \rangle - \overline{M_2} - \overline{\overline{M_2}},
\tag{31d}
$$

and inserting the correlation function (18) into Eq. (30) we obtain

$$
\begin{aligned}
V(t, t_2, \tau, t_1) &= \beta \Bigg\{ 1 - \frac{1}{2} K_0 \Big[t - \Big(2\tau + t_2 - \frac{t_1}{2} \Big) \Big]^2 \\
&\quad - \sum_i K_i \tau_{ci}^2 R_i(t, t_2, \tau, t_1, \tau_{ci}) + \cdots \Bigg\} \\
&= \beta \exp \Bigg\{ - \frac{1}{2} K_0 \Big[t - \Big(2\tau + t_2 - \frac{t_1}{2} \Big) \Big]^2 \\
&\quad - \sum_i K_i \tau_{ci}^2 R_i(t, t_2, \tau, t_1, \tau_{ci}) \Bigg\},
\end{aligned}
\tag{32}
$$

where

$$
\begin{aligned}
R_i(t, t_2, \tau, t_1, \tau_{ci}) = &-\frac{7}{4} + \frac{t}{\tau_{ci}} - \frac{3t_1}{4\tau_{ci}} - \frac{t_2}{\tau_{ci}} - \frac{1}{4} \exp\left(-\frac{t_1}{\tau_{ci}}\right) \\
&- \exp\left(-\frac{t_2}{\tau_{ci}}\right) - \frac{1}{2} \exp\left(-\frac{t}{\tau_{ci}}\right) \\
&+ \frac{1}{2} \exp\left(-\frac{\tau - t_1}{\tau_{ci}}\right) - \frac{1}{2} \exp\left(-\frac{t - t_1}{\tau_{ci}}\right) \\
&+ \frac{1}{2} \exp\left(-\frac{\tau + t_2}{\tau_{ci}}\right) + \exp\left(-\frac{t - \tau}{\tau_{ci}}\right) \\
&+ \exp\left(-\frac{t - \tau - t_2}{\tau_{ci}}\right) + \frac{1}{2} \exp\left(-\frac{\tau}{\tau_{ci}}\right) \\
&+ \frac{1}{2} \exp\left(-\frac{\tau + t_2 - t_1}{\tau_{ci}}\right).
\end{aligned}
\tag{33}
$$

The temperature dependence of time position of the maximum of the solid echo signal is shown in Fig. 5.
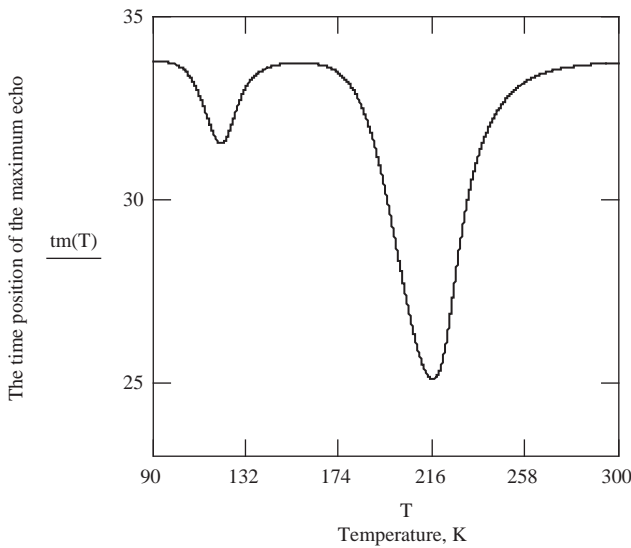

Fig. 5. Temperature dependence of time position (t_m, μs) of the maximum of the solid echo signal. The graph obtained from Eq. (33) for the same parameters as in Figs. 2–4; $\tau = 16\,\mu s$, $t_i = 3.6\,\mu s$.

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