

Nuclear Spin Relaxation by Translational Diffusion. III. Spin-Spin Relaxation

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Theory relating spin-lattice relaxation times to diffusion rates has been extended to include the relation of spin-spin relaxation times to diffusion rates. Certain tables presented earlier have been corrected to bring them into agreement with presently accepted theory.

IN two previous articles hereafter referred to as I and II,² the general problem of nuclear spin relaxation by diffusion was discussed. Results were obtained for the spin-lattice relaxation time T_1 for lattice diffusion describable by a random walk to nearest neighbor positions in fcc and bcc lattices. In this paper the extension to the spin-spin relaxation time T_2 is made. This extension is possible because in the time since I and II were presented, a more definite theoretical expression for T_2 has been developed.³ In this intervening time the theoretical expression for T_1 has also been revised⁴ so that certain tabular material appearing in I and II is slightly incorrect, and the corrected results will also be presented.

The expressions given by theory for the spin-lattice relaxation time T_1 and the spin-spin relaxation time T_2 are, respectively,

$$T_1^{-1} = \frac{3}{4}\gamma^4\hbar^2 I(I+1)[2S_1(\omega_0) + 2S_2(2\omega_0)], \quad (1)$$

$$T_2^{-1} = \frac{3}{2}\gamma^4\hbar^2 I(I+1)\left[\frac{1}{4}S_0(0) + \frac{5}{2}S_1(\omega_0) + \frac{1}{4}S_2(2\omega_0)\right], \quad (2)$$

where, for example,

$$S_0(\omega) = \int_{-\infty}^{\infty} e^{i\omega t} k_0(t) dt, \quad (3)$$

$$k_0(t) = \sum_i \langle F_{ij}^{(0)}(t') F_{ij}^{(0)}(t'+t) \rangle_{av}(t'), \quad (4)$$

$$F_{ij}^{(0)}(t) = (1 - 3 \cos^2 \theta_{ij}) / r_{ij}^3, \quad (5)$$

and where r_{ij} , θ_{ij} , and φ_{ij} are the time varying spherical coordinates of spin j relative to spin i , and ω_0 is the Larmor frequency. $S_1(\omega)$ and $S_2(\omega)$ are defined in a similar manner in I. The expression for T_1 given in I had the factor unity instead of 2 before $S_2(\omega_0)$ in (1), and the factor 2 has since been shown to be correct.

In I it is shown that

$$S_1(\omega) = [8\pi c n \tau / (15k^3 l^3)] G(k, y) \quad (6)$$

and that

$$S_2(\omega) = 4S_1(\omega). \quad (7)$$

¹ H. C. Torrey, Phys. Rev. **92**, 962 (1953).
² H. C. Torrey, Phys. Rev. **96**, 690 (1954).
³ I. Solomon and N. Bloembergen, J. Chem. Phys. **25**, 261 (1956).
⁴ R. Kubo and K. Tomita, J. Phys. Soc. Japan **9**, 888 (1954).

It can also be shown following the outline in I that

$$S_0(\omega) = 6S_1(\omega). \quad (8)$$

In (6) n is the number of lattice sites per unit cell, c is the number of atoms per lattice site, τ is the time between jumps and is given by $l^2/6D$, k is a normalization factor (given in I and II), l is the jump distance, D is the macroscopic diffusion coefficient, y is $\omega\tau/2$, and

$$G(k, y) = \int_0^{\infty} J_{3/2}^2(kx) \frac{1 - (\sin x)/x}{[1 - (\sin x)/x]^2 + y^2} \frac{dx}{x}. \quad (9)$$

Values of $G(k, y)$ are tabulated below in Table I for fcc and bcc lattices, respectively. These values, along with those of $\varphi(k, y)$ and $R(k, y)$ defined below, were computed on the NAREC computer at the U. S. Naval Research Laboratory and are accurate to at least three significant figures. Methods used in simplifying the calculation of $G(k, y)$ are given in the Appendix.

For the purposes of condensed notation, Eqs. (1) and (2) can be rewritten

$$\begin{aligned} T_1^{-1} &= C \varphi(k, y), \\ T_2^{-1} &= C \left[\frac{3}{2} y G(k, 0) + \Omega(k, y) \right], \end{aligned} \quad (10)$$

where

$$C = \gamma^4 \hbar^2 I(I+1) 8\pi n c / (5k^3 l^3 \omega), \quad (12)$$

$$\varphi(k, y) = y G(k, y) + 4y G(k, 2y), \quad (13)$$

$$\Omega(k, y) = \frac{5}{2} y G(k, y) + y G(k, 2y). \quad (14)$$

For convenience, $\varphi(k, y)$ is given also in Table I. $\Omega(k, y)$ is not as useful to the experimenter, and is not tabulated. Its further use will be indicated below.

As ωt becomes much less than unity, it is to be expected that $T_2 = T_1$. This can be shown to be the case if $G(k, 0)$ is used in all the spectral density functions S as shown in (6). Then

$$T_2^{-1} = T_1^{-1} = 5C y G(k, 0). \quad (15)$$

Another region of interest is that within the limits $\omega t \gg 1$ and $\sigma_0 k \ll 1$ (where σ_0 is the square root of the rigid lattice second moment expressed in sec^{-1}), i.e., the region below the T_1 minimum and before the onset

TABLE I. The functions $G(k,y)$, $\varphi(k,y)$, and $R(k,y)$ evaluated at selected values of δ for body-centered cubic and face-centered cubic lattices.

y	$k=0.76293$ (bcc lattice)				$k=0.74280$ (fcc lattice)			
	$G(k,y)$	$G(k,2y)$	$\varphi(k,y)$	$R(k,y)$	$G(k,y)$	$G(k,2y)$	$\varphi(k,y)$	$R(k,y)$
0	0.6369		0	0.7000	0.6145		0	0.7000
0.025	0.5557		0.06609	0.7229	0.5394		0.06430	0.7218
0.05	0.5220		0.1209	0.7356	0.5081		0.1181	0.7340
0.1	0.4740		0.2097	0.7584	0.4635		0.2061	0.7559
0.15	0.4371		0.2778	0.7810	0.4289		0.2742	0.7778
0.2	0.4059		0.3295	0.8043	0.3994		0.3264	0.8006
0.25	0.3784		0.3680	0.8285	0.3734		0.3657	0.8243
0.3	0.3537		0.3957	0.8534	0.3498		0.3942	0.8489
0.35	0.3312		0.4148	0.8786	0.3282		0.4142	0.8740
0.4	0.3104		0.4271	0.9040	0.3082		0.4273	0.8992
0.45	0.2912		0.4341	0.9291	0.2896		0.4349	0.9242
0.5	0.2733		0.4370	0.9536	0.2723		0.4384	0.9487
0.55	0.2567		0.4368	0.9775	0.2561		0.4387	0.9726
0.6	0.2413		0.4341	1.000	0.2411		0.4365	0.9955
0.65	0.2269		0.4298	1.022	0.2269		0.4325	1.017
0.7	0.2135		0.4241	1.042	0.2138		0.4272	1.038
0.8	0.1893		0.4102	1.080	0.1900		0.4137	1.076
0.9	0.1684		0.3945	1.114	0.1692		0.3983	1.110
1.	0.1501		0.3781	1.143	0.1511		0.3822	1.139
1.1	0.1343	0.04865	0.3618	1.168	0.1353	0.04934	0.3660	1.165
1.2	0.1205	0.04194	0.3460	1.190	0.1216	0.04255	0.3502	1.187
1.3	0.1085	0.03647	0.3308	1.209	0.1096	0.03702	0.3350	1.207
1.4	0.09809		0.3164	1.226	0.09911		0.3205	1.233
1.6	0.08085	0.02510	0.2900	1.253	0.08180	0.02550	0.2941	1.251
1.8	0.96749	0.02019	0.2668	1.274	0.06835	0.02051	0.2707	1.272
2.	0.05699		0.2465	1.290	0.05776		0.2502	1.288
2.25	0.04684	0.01324	0.2245	1.305	0.04750	0.01346	0.2280	1.304
2.5	0.03907		0.2058	1.317	0.03965		0.2091	1.316
2.8	0.03197	0.008689	0.1868	1.328	0.03247	0.008837	0.1898	1.327
3.	0.02824		0.1759	1.333	0.02868		0.1787	1.332
3.5	0.02127		0.1531	1.344	0.02162		0.1557	1.343
4.	0.01656		0.1354	1.350	0.01683		0.1377	1.350
5.	0.01081		0.1097	1.359	0.01100		0.1116	1.359
6.	0.007598	0.001936	0.09207	1.364	0.007728	0.001970	0.09367	1.363
7.	0.005620		0.07925	1.366	0.005717		0.08064	1.366
8.	0.004322	0.001092	0.06954	1.368	0.004397	0.001111	0.07076	1.366
10.	0.002781		0.05582	1.370	0.002829		0.05680	1.370
14.	0.001425	0.0003577	0.03998	1.372	0.001450	0.0003640	0.04069	1.372
20.	0.0007003		0.02803	1.373	0.0007126		0.02852	1.373
30.	0.0003116		0.01870	1.374	0.0003171		0.01903	1.374
40.	0.0001754	0.0000439	0.01403	1.374	0.0001785	0.0000446	0.01428	1.374
60.	0.0000780	0.0000195	0.009357	1.374	0.0000793	0.0000198	0.009522	1.374
>80.	$0.2808/y^2$		$0.5615/y$	1.375	$0.02857/y^2$		$0.5714/y$	1.375

of the rigid lattice behavior. In this region

$$T_2^{-1} = \frac{3}{2} C \gamma G(k, 0), \quad (16)$$

which is just $\frac{3}{10}$ the value given by (15).

Where T_2 data are available in the vicinity of the T_1 minimum it will be desired to remove the "hump" which will appear in the semilog plot of T_2 versus reciprocal temperature in the range where transition is occurring between the two asymptotic regions described by (15) and (16). Stated another way, it will be desired

to make the customary T_1 correction. A procedure for doing this is indicated here. Define a quantity T_2' as

$$(T_2')^{-1} = \frac{3}{2} C \gamma G(k, 0). \quad (17)$$

It can be seen that $(T_2')^{-1}$ is a linear function of y , and does not have the "hump." Then

$$(T_2')^{-1} = T_2^{-1} - R T_1^{-1}, \quad (18)$$

where

$$R = \Omega(k, y) / \varphi(k, y). \quad (19)$$

This ratio R is also presented in Table I, since it will probably be of most direct use to the experimenter. where

$$\begin{aligned}
 h_0(y) &= (1+y^2)^{-1}, \\
 h_1(y) &= (1-y^2)/(1+y^2)^2, \\
 h_2(y) &= (1-3y^2)/(1+y^2)^3, \\
 g_0(k) &= \frac{1}{3}, \\
 g_1(k) &= \frac{1}{3} - \frac{1}{4}k^{-1} + k^3/48, \\
 g_2(k) &= k^2/15,
 \end{aligned}
 \tag{A4}$$

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APPENDIX

The integral in Eq. (9) for $G(k,y)$ converges slowly. It has been recast as follows:

$$G(k,y) = \text{Re} \sum_0^\infty [(1-iy)^{-1}]^{n+1} g_n(k), \tag{A1}$$

where

$$g_n(k) = \int_0^\infty J_{3/2}^2(kx) [(\sin x)/x]^n x^{-1} dx. \tag{A2}$$

Write (A1) as

$$\begin{aligned}
 G(k,y) &= g_0(k)h_0(y) + g_1(k)h_1(y) \\
 &\quad + g_2(k)h_2(y) + I(k,y), \tag{A3}
 \end{aligned}$$

under the conditions that $\frac{1}{2} < k < 1$. Also

$$I(k,y) = \sum_{n=3}^\infty g_n(k) \frac{\cos[(n+1) \tan^{-1}y]}{[(1+y^2)^{1/2}]^{n+1}} \tag{A5}$$

$$\begin{aligned}
 &= \frac{1-3y^2}{(1+y^2)^3} \int_0^\infty J_{3/2}^2(k,x) \\
 &\quad \times \frac{1 - (\sin x)/x - y^2(3-y^2)/(1-3y^2)}{[1 - (\sin x)/x]^2 + y^2} \\
 &\quad \times [(\sin x)/x]^3 x^{-1} dx. \tag{A6}
 \end{aligned}$$

The integral $I(k,y)$ converges more rapidly than $G(k,y)$ and was used in the calculations. Integration was done using Simpson's rule. The upper limit found sufficient was 4π .