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NMR magnetic dipolar spectral density functions for two-dimensional lattice diffusion

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Abstract. NMR magnetic dipolar spectral density functions are obtained for some lattice diffusion models for two-dimensional lattice diffusion and compared with the results for the BPP and continuum models. The systems considered are dipolar interactions between spins diffusing in a plane, and interactions between diffusing spins in a plane with fixed spins in a separate parallel plane. Numerical results and analytic approximations are obtained for spins diffusing on square lattices. The BPP model is unsatisfactory in both magnitude and functional form in two-dimensional systems. The continuum and lattice diffusion models agree for interactions between well separated planes, but there are significant differences between the continuum and lattice models otherwise. Results for the longitudinal spin relaxation rates in the laboratory and rotating frames are obtained for square lattices, and show a strong dependence on the direction of the applied magnetic field relative to the crystal axes.

1. Introduction

The theory of nuclear spin relaxation due to fluctuating magnetic dipolar interactions involves, in the weak-collision limit, spectral density functions, which depend on the nature of the fluctuations. If the time dependence of the dipolar interactions is due to translational diffusion of the spins it is well known that the functional form of the spectral density functions depends on the dimensionality of the system (see, for example, Sholl 1981), especially in the rapid-diffusion limit corresponding to high temperatures or low resonant frequencies. In the case of interacting spins undergoing two-dimensional diffusion in a plane the spectral density functions depend on the frequency ω according to $\log(1/\omega)$ in the low-frequency limit under very general conditions.

The evaluation of the spectral density functions for two-dimensional systems has been considered for continuum diffusion models by Avogadro and Villa (1977) and Korb *et al* (1983, 1984, 1987b) for the case where the dipolar interactions are all in a plane. The extension of this theory to the diffusing spins in a plane interacting with spins in a separate parallel plane has been treated by Korb *et al* (1987a) and Neue (1988). The continuum diffusion models are appropriate for systems in which the mobile spins behave like two-dimensional liquids, but may not be good approximations for spins undergoing diffusion on a lattice. The high-frequency form of the spectral density functions for spins diffusing on square and hexagonal lattices has been derived by MacGillivray and Sholl (1985a, b) but there are no results available for discrete lattice diffusion over the entire frequency range.

The aim of the present work is to calculate the spectral density functions and nuclear spin relaxation rates over the complete frequency range for some lattice diffusion models and to compare the results to those for continuum diffusion models and the BPP model (Bloembergen *et al* 1948). The general theory is developed for arbitrary two-dimensional structures and is applied specifically to the case of a square lattice. The cases of spins interacting with each other in the same plane and of spins in one plane interacting with spins in a separate parallel plane are both considered. The form of the dependence of the spectral density functions and relaxation rates on the direction of the applied magnetic field relative to the crystal axes is more involved for the square lattice than for the continuum model, and results for this angular dependence are presented.

2. Spectral density functions

The spectral density functions relevant to nuclear spin relaxation due to magnetic dipolar interactions, for both like- and unlike-spin interactions, are (Abragam 1961, Sholl 1981)

$$J^{(p)}(\omega) = cd_p^2 \sum_{\alpha,\beta} \frac{Y_{2p}^*(\Omega'_\alpha)}{r_\alpha^3} \frac{Y_{2p}(\Omega'_\beta)}{r_\beta^3} P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \omega) \tag{1}$$

where $d_0^2 = 16\pi/5$, $d_1^2 = 8\pi/15$, $d_2^2 = 32\pi/15$, $Y_{2p}(\Omega')$ are spherical harmonics normalized to unity, $\boldsymbol{r}_\alpha = (r_\alpha, \Omega'_\alpha)$ are vectors separating the interacting spins and c is the probability of finding a spin at $\boldsymbol{r}_\alpha$ relative to one at the origin. The function $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \omega)$ is the Fourier transform

$$P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \omega) = 2\int_0^\infty P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t) \cos \omega t \, \mathrm{d}t \tag{2}$$

of $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t)$, which is the probability of a pair of spins being separated by $\boldsymbol{r}_\beta$ a time t after they were separated by $\boldsymbol{r}_\alpha$. The directions Ω'_α of the spherical harmonics are relative to the direction of the applied magnetic field.

The dependence of $J^{(p)}(\omega)$ on the orientation of the crystal with respect to the magnetic field direction can be expressed, in terms of trigonometric functions of the polar angles (θ, ϕ) of the field direction relative to crystal axes and functions $J_{pp'}(\omega)$ defined for p and $p' = -2$ to 2, by (Sholl 1986)

$$J_{pp'}(\omega) = c \sum_{\alpha,\beta} \frac{Y_{2p}^*(\Omega_\alpha)}{r_\alpha^3} \frac{Y_{2p'}(\Omega_\beta)}{r_\beta^3} P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, \omega) \tag{3}$$

where the directions of the spherical harmonics are now relative to axes fixed in the crystal. The z direction will be chosen to be the normal to the plane of the diffusing spins.

The maximum number of independent non-zero parameters needed to specify $J^{(p)}(\omega)$ for each frequency is 15, and crystal symmetry reduces this number (Sholl 1986). If the z axis is a sixfold rotation axis, or if there is circular symmetry about the z axis, as is the case for a continuum diffusion model, only the three (real) diagonal elements of $J_{pp'}(\omega)$ are non-zero and $J^{(p)}(\omega)$ depends only on θ according to

$$d_p^{-2} J^{(p)}(\omega) = J_{pp} + B_p \sin^2\theta + C_p \sin^4\theta \tag{4}$$

$$B_0 = 3(J_{11} - J_{00}) \qquad B_1 = \tfrac{1}{2}(3J_{00} - 5J_{11} + 2J_{22}) \qquad B_2 = J_{11} - J_{22} \tag{5}$$

$$C_0 = \tfrac{3}{4}(3J_{00} - 4J_{11} + J_{22}) \qquad C_1 = -\tfrac{2}{3}C_0 \qquad C_2 = \tfrac{1}{6}C_0. \tag{6}$$

If the z axis is a threefold or fourfold rotation axis $J^{(p)}(\omega)$ also depends on ϕ, and there are additional terms to (4) given by

$$3D_p \sin^3\theta \cos\theta\, \Re(e^{3i\phi} J^*_{-12}) \qquad \text{threefold axis} \tag{7}$$

$$\tfrac{3}{4} D_p \sin^4\theta\, \Re(e^{4i\phi} J^*_{-22}) \qquad \text{fourfold axis} \tag{8}$$

where $D_0 = 1$, $D_1 = -\frac{2}{3}$ and $D_2 = \frac{1}{6}$.

The number of independent (real) parameters is therefore three for a sixfold rotation axis or circular symmetry, and five for a threefold or fourfold rotation axis. If the dipolar interactions are restricted to the plane of diffusion, J_{11} and J_{-12} are zero because the spherical harmonics in (3) become zero. There are then only two parameters, (J_{00}, J_{22}), for threefold or sixfold rotation axes, and four parameters, (J_{00}, J_{22}, complex J_{-22}), for a fourfold rotation axis. These results for the continuum diffusion in a plane are consistent with the angular expressions of Avogadro and Villa (1977) and the results for a fourfold axis are consistent with the case $\phi = 0$ considered by MacGillivray and Sholl (1985a). (In equation (3.7) in the latter paper, $f_2^{(0)}(\theta)$ should be $\frac{9}{4}\sin^4\theta$.)

The spherical average over all magnetic field directions $\langle J^{(p)}(\omega)\rangle$ of the spectral density functions in all cases is

$$\langle J^{(p)}(\omega)\rangle = \frac{d_p^2}{5}(J_{00} + 2J_{11} + 2J_{22}). \tag{9}$$

A circular average about the z axis gives the expression in (4) in all cases, since the additional terms (7) and (8) average to zero.

Since the relaxation rates are linear combinations of the spectral density functions (Abragam 1961) the relaxation rates have the same functional form as $J^{(p)}(\omega)$ for their orientation dependence on the magnetic field direction, and this is also the case for the appropriate averages over magnetic field directions.

In the weak-collision limit the experimentally measurable relaxation rates can be written as linear combinations of the spectral density functions $J^{(p)}(\omega)$. For example, for like-spin dipolar interactions the longitudinal relaxation rates, R_1 and $R_{1\rho}$ in the laboratory and rotating frames, respectively, are (see, for example, Kelly and Sholl 1992)

$$R_1 = 4C[J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)] \tag{10}$$

$$R_{1\rho} = C[J^{(0)}(2\omega_1) + 10J^{(1)}(\omega_0) + J^{(2)}(2\omega_0)] \tag{11}$$

where $C = \frac{3}{8}\gamma^4\hbar^2 I(I+1)(\mu_0/4\pi)^2$, γ is the gyromagnetic ratio of the nuclear spin with spin quantum number I, and ω_0 and ω_1 are the Larmor frequencies of the spins in the applied static and oscillating magnetic fields, respectively. The spectral density functions $J^{(p)}(\omega)$ are expressed in terms of $J_{pp'}(\omega)$ by (4)–(8), and the $J_{pp'}(\omega)$ are defined relative to the crystal axes by (3).

It is convenient to discuss and present the results in terms of the dimensionless function $g_{pp'}(\omega\tau)$, which is related to $J_{pp'}(\omega)$ by

$$J_{pp'}(\omega) = c\tau S_{pp'}\, g_{pp'}(\omega\tau) \tag{12}$$

where τ is a characteristic correlation time of the diffusion, which is discussed in section 3, and $S_{pp'}$ is the lattice summation

$$S_{pp'} = \sum_\alpha \frac{Y^*_{2p}(\Omega_\alpha) Y_{2p'}(\Omega_\alpha)}{r_\alpha^6}. \tag{13}$$

The values of $S_{pp'}$ depend only on the geometry of the spin system, and values are given in section 4.

3. Diffusion models

The systems to be considered are spins diffusing on two-dimensional lattices by random jumps to vacant nearest-neighbour lattice sites. The dipolar interaction may be between like spins undergoing relative diffusion on the same lattice, or between unlike spins where the dipolar interaction is between a diffusing spin in a plane and a lattice of fixed spins in the same plane or another parallel plane or planes. For unlike-spin interactions the probability function $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t)$ will be of the form

$$P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t) = P(\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta, t) \tag{14}$$

if the fixed spins do not influence the diffusion of the moving spins. This is not the case for the relative diffusion of like spins on the same lattice, since each of a pair of diffusing spins will then interfere with the diffusion of the other, even in the limit of low spin concentration on the lattice corresponding to just two spins.

3.1. BPP model

The BPP model for the spectral density functions is based on an approximation for $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t)$ that corresponds to the pair of spins maintaining their relative separation for a mean time τ and assuming that the correlation in their dipolar interaction is completely destroyed when a jump of one of the spins occurs. It is therefore equivalent to choosing $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t)$ to be $\delta_{\alpha\beta}\exp(-t/\tau)$. The parameter τ is τ_c for the unlike-spin case, where only one spin is mobile, with a mean time of τ_c between jumps, and is $\tau_c/2$ when either spin can jump, as in the like-spin case. The resulting dimensionless spectral density functions $g_{pp'}(\omega\tau)$ for the BPP model are zero if $S_{pp'} = 0$, and otherwise are

$$g_{pp'}(\omega\tau) = \frac{2}{1 + (\omega\tau)^2} \tag{15}$$

which are independent of p, p', the crystal structure and any microscopic details of the diffusion process other than τ. This model is widely used in analysing nuclear spin relaxation data.

3.2. Continuum model

In the limit of large distances and long times the lattice diffusion may be described by the continuum diffusion expression in two-dimensions, which is

$$P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t) = \frac{1}{4\pi Dt}\exp\left(\frac{-(\boldsymbol{r}_\alpha - \boldsymbol{r}_\beta)^2}{4Dt}\right) \tag{16}$$

where the diffusion constant D is related to the lattice diffusion by $D = a^2/(4\tau_c)$, where a^2 is the mean-square jump length and τ_c is the mean time between jumps of a spin. This is the model considered by Neue (1988) for interactions between unlike spins, where one of the two spin types is fixed while the other diffuses on a second plane a distance z from the first. The resulting spectral density functions can be written in the form

$$J_{pp'}(\omega) = \delta_{pp'}\begin{pmatrix} 4 \\ 2-|p| \end{pmatrix}\frac{5n\tau}{6z^2a^2}C(\omega\tau_z) \tag{17}$$

$$C(u) = \int_0^\infty x^5\left(x^4 + \frac{9u^2}{4}\right)^{-1}\exp(-2x)\,\mathrm{d}x \tag{18}$$

where n is the surface density of lattice sites and τ_z is a parameter with the dimensions of time defined by

$$\tau_z = \frac{8z^2\tau}{3a^2}. \tag{19}$$

The parameter τ in these expressions is τ_c if only one spin is diffusing, and becomes $\tau_c/2$ if both spins are diffusing. In the limit of large $\omega\tau_z$ ($\omega\tau z^2 \to \infty$), $C(\omega\tau_z) = 5/[6(\omega\tau_z)^2]$ so that

$$J_{pp'}(\omega) = \delta_{pp'}\left(\frac{4}{2-|p|}\right)\frac{25na^2\tau}{256}\frac{1}{z^6}\frac{1}{(\omega\tau)^2} \tag{20}$$

in this limit. For small values of $\omega\tau_z$ ($\omega\tau z^2 \ll 1$) the $J_{pp}(\omega)$ are linear in $\omega\tau$ and

$$J_{pp'}(\omega) \simeq \delta_{pp'}\left(\frac{4}{2-|p|}\right)\frac{5n\tau}{6a^2}\left(\frac{1}{4z^2} - \frac{\pi}{a^2}\omega\tau\right). \tag{21}$$

The expression (17) diverges as $z \to 0$ since the model then allows the unphysical condition that the two interacting spins can occupy the same site. An approximation for $z = 0$ that overcomes this difficulty is to limit the starting and finishing separations of the spins to regions outside circles of radius d. A similar analysis to Neue then gives (Avogadro and Villa 1977)

$$J_{pp'}(\omega) = \delta_{pp'}A_p\frac{4\tau n}{d^2a^2}C_p(\omega\tau_D) \tag{22}$$

$$C_p(u) = \int_0^\infty x^5(x^4+u^2)^{-1}\left(\int_x^\infty \frac{J_{|p|}(y)}{y^2}\,\mathrm{d}y\right)^2\mathrm{d}x \tag{23}$$

where $A_0 = 5/4$, $A_{\pm1} = 0$, $A_{\pm2} = 15/8$, $\tau_D = 4\tau d^2/a^2$ and the $J_{|p|}(y)$ are Bessel functions. The parameter τ is again τ_c for one spin diffusing and $\tau_c/2$ for both spins diffusing. More sophisticated continuum diffusion models have been considered by Korb *et al* (1983, 1984, 1987a, b, 1990).

3.3. Random walk model

A general approach to evaluating the spectral density functions for discrete lattice diffusion is to use a reciprocal space formalism (Fedders and Sankey 1978, Barton and Sholl 1980) in which

$$J_{pp'}(\omega) = \left(\frac{A}{4\pi^2}\right)^2\iint \mathrm{d}\boldsymbol{q}\,\mathrm{d}\boldsymbol{q}'\,T_p^*(\boldsymbol{q},\boldsymbol{j},z)T_{p'}(\boldsymbol{q}',\boldsymbol{j},z)P(\boldsymbol{q},\boldsymbol{q}',\omega) \tag{24}$$

where the integrals are over the first Brillouin zone of the two-dimensional reciprocal lattice, A is the area of the two-dimensional unit cell, $P(\boldsymbol{q},\boldsymbol{q}',\omega)$ is the temporal and spatial Fourier transform of $P(\boldsymbol{r}_\alpha,\boldsymbol{r}_\beta,t)$ and

$$T_p(\boldsymbol{q},\boldsymbol{j},z) = \sum_l \frac{Y_{2p}(\Omega_\alpha)}{r_\alpha^3}\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{r}_\alpha) \tag{25}$$

where $r_\alpha = l + j + z\hat{k}$. The vectors l are two-dimensional lattice vectors (in the xy plane) and $j + z\hat{k}$ is the relative displacement of a planar lattice of fixed spins from the planar lattice of diffusing spins, where z is the separation between the planes and j is a planar vector characterizing the relative displacement of the lattices parallel to the planes. For like-spin dipolar interactions in a plane, j and z are both zero and the term $l = 0$ must be omitted from the summation in (25). An efficient method of evaluating lattice summations of the form of $T_p(q, j, z)$ is to use the Poisson summation formula (Barton and Sholl 1980) and the resulting expressions for the two-dimensional summations are given in the appendix. A particular lattice diffusion model will determine $P(q, q', \omega)$, and $J_{pp'}(\omega)$ can then be evaluated using (24) and the expressions in the appendix. The symmetry of the calculated $J_{pp'}(\omega)$ will be as discussed in section 2.

A simple model of the diffusion of a spin is that it follows a random walk with a mean time of τ_c between jumps. Random walk theory (Barber and Ninham 1970) and equation (14) then give the expression

$$P(q, q', \omega) = \frac{2\tau\delta_{q,q'}[1 - \phi(q)]}{[1 - \phi(q)]^2 + (\omega\tau)^2} \tag{26}$$

where $\tau = \tau_c$ for one spin diffusing and $\tau = \tau_c/2$ for both spins diffusing, $\phi(q)$ is the lattice structure factor, defined by

$$\phi(q) = \sum_k w_k \exp(\mathrm{i}q \cdot r_k) \tag{27}$$

and w_k is the probability that the jump of a spin from the origin will be to r_k. For nearest-neighbour jumps on a square lattice with lattice parameter a

$$\phi(q) = \tfrac{1}{2}(\cos q_1 a + \cos q_2 a). \tag{28}$$

In the limit of small $\omega\tau$, which corresponds to long-range diffusion, and as $z \to \infty$ in such a way that $\omega\tau z^2 \to 0$, the spectral density functions of the random walk and the continuum models are equal. In these limits, (21) for the continuum model of diffusion is also valid for the random walk model.

If a fraction c of the lattice sites are occupied by diffusing spins the mean time τ_c between jumps of a spin is $\tau_0/(1-c)$, where τ_0 is the mean time between jumps of a spin if it is the only spin on the lattice. For unlike-spin dipolar interactions between fixed spins and diffusing spins the random walk model is exact in the limit $c \to 0$ and will be a reasonable approximation at other concentrations, except in the limit $c \to 1$ since the diffusion is then controlled by the random walks of vacancies. In three dimensions the encounter model (Wolf 1979, MacGillivray and Sholl 1986, Sholl 1992) is then valid, but this will not be applicable to two-dimensional systems. This is because an encounter cannot then be defined and Brummelhuis and Hilhorst (1989) have recently analysed the random walk theory for the limit of $c \to 1$ in two-dimensional systems.

3.4. *Mean field model*

The random walk model for like-spin dipolar interactions between two spins diffusing on the same lattice allows the unphysical possibility of the pair of spins both occupying the same site and therefore requires exclusion of the term $l = 0$ in expression (25). It is therefore not rigorously correct even in the limit $c \to 0$. An improved theory, which will be referred to as the mean field model, is to rigorously take into account the site-blocking effects of the two spins, but to take the effects of the other spins into account only through the mean time τ_c between jumps, as for the random walk model. This mean field model will again not be valid in the limit $c \to 1$, but is exact in the limit $c \to 0$. The results of a comparison between the random walk and mean field models for the spectral density functions in cubic crystals (Barton and Sholl 1980) suggested that the difference between the results for these models increases as the lattice coordination number decreases. It would therefore be expected that the difference between the $J^{(p)}(\omega)$ for the two models would be significant for planar systems, which can have low coordination numbers.

The evaluation of $P(\boldsymbol{q}, \boldsymbol{q}', \omega)$ for the mean field model in two dimensions is similar to that in three dimensions (Barton and Sholl 1980). Fourier transforming the rate equation for $P(\boldsymbol{r}_\alpha, \boldsymbol{r}_\beta, t)$ gives an integral equation for $P(\boldsymbol{q}, \boldsymbol{q}', \omega)$ and the solution of this equation for a square lattice is (Stephenson 1993)

$$P(\boldsymbol{q}, \boldsymbol{q}', \omega) = \frac{2\tau\delta_{\boldsymbol{q},\boldsymbol{q}'}[1-\phi(\boldsymbol{q})]}{[1-\phi(\boldsymbol{q})]^2 + (\omega\tau)^2} + \Re\left(d_0(\boldsymbol{q}, \omega) d_0(\boldsymbol{q}', \omega) \sum_{l=1}^{2} \frac{F_l(\boldsymbol{q}) F_l(\boldsymbol{q}')}{B_l(\omega)}\right) \tag{29}$$

where

$$d_0(\boldsymbol{q}, \omega) = \frac{\tau}{[1-\phi(\boldsymbol{q})] - \mathrm{i}(\omega\tau)}$$

$$F_1(\boldsymbol{q}) = 2 - \cos q_1 a - \cos q_2 a \qquad F_2(\boldsymbol{q}) = \cos q_1 a - \cos q_2 a$$

$$B_1(\omega) = 2\tau - \frac{A}{4\pi^2} \int \mathrm{d}\boldsymbol{q}\, d_0(\boldsymbol{q}, \omega)(2 - 4\cos q_1 a + \cos^2 q_1 a + \cos q_1 a \cos q_2 a)$$

$$B_2(\omega) = 2\tau - \frac{A}{4\pi^2} \int \mathrm{d}\boldsymbol{q}\, d_0(\boldsymbol{q}, \omega)(\cos^2 q_1 a - \cos q_1 a \cos q_2 a)$$

where $\tau = \tau_c/2$ and the integrals in the above expressions for the $B_l(\omega)$ are over the first Brillouin zone of the two-dimensional reciprocal lattice. The spectral density functions for the mean field model are then obtained from (24) and (25).

4. Results

Some numerical results are presented below for the spectral density functions and relaxation rates for diffusion on a square lattice. The spectral density functions $J_{pp'}(\omega)$ are related to their dimensionless forms $g_{pp'}(\omega\tau)$ by (12), and the values of the lattice summations $S_{pp'}$ for square lattices are given in table 1. For simplicity, the only cases to be considered are unlike-spin dipolar interactions between diffusing spins in one plane and fixed spins in a parallel plane, where the planes are separated by $z > 0$, and like-spin dipolar interactions between spins diffusing in the same plane. Other similar like- and unlike-spin examples, including systems for which $\boldsymbol{j}$, the relative displacement of the planes parallel to the planes, is non-zero are easily calculated and show similar qualitative features but are not considered here.

Table 1. Values of the lattice summations $S_{pp'}$, defined by (13), for a square lattice and for $z = 0$, a and $10a$ where a is the lattice parameter.

	$z = 0$	$z = a$	$z = 10a$
$a^6 S_{00}$	0.4634	0.4132	2.344×10^{-5}
$a^6 S_{11}$	0.0	0.1015	1.562×10^{-5}
$a^6 S_{22}$	0.6951	0.03851	3.905×10^{-6}
$a^6 S_{-22}$	0.5286	0.01070	-3.722×10^{-10}

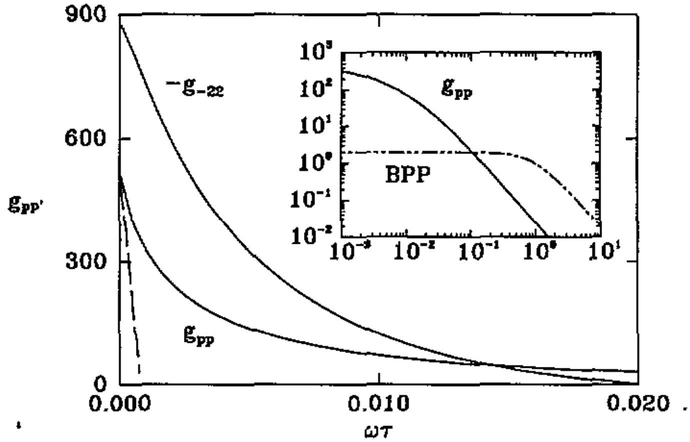

Figure 1. The functions $g_{pp'}(\omega\tau)$ for the random walk and BPP models for dipolar interactions between diffusing spins and fixed spins on square lattices separated by $z = 10a$. The BPP results are independent of p and p'. The broken curve for small $\omega\tau$ shows the limiting linear form of $g_{pp}(\omega\tau)$ for the random walk model.

4.1. Separate planes

The non-zero independent spectral density functions for square lattices with $z > 0$ and $j = 0$ are $g_{pp}(\omega\tau)$ for $p = 0, 1, 2$ and the real part of $g_{-22}(\omega\tau)$. These functions are shown in figure 1 for $z = 10a$ for the BPP and random walk models. The random walk results for $g_{pp}(\omega\tau)$ are the same for $p = 0, 1, 2$ to within 0.04% for this value of z. All of the functions are proportional to $(\omega\tau)^{-2}$ for large $\omega\tau$, as a result of this limit depending only on the details of the probabilities of no jump or one jump of a spin occurring in a time t. The range of $\omega\tau$ over which this limit is valid is, however, very different for the BPP and random walk models and increases with increasing z for the random walk model. This result is a consequence of the assumption in the BPP model that the correlation in dipolar interactions is completely destroyed when a jump of a spin occurs. This becomes a poor approximation for large z because the jump of a spin then only involves a small change in the dipolar interaction between the spins and the random walk model includes the effect of this change correctly. The maxima in the relaxation rates occur at much smaller values of $\omega\tau$ for the random walk model than for the BPP model as z increases, as a result of this difference between the models. The BPP model is also clearly a poor approximation, both in magnitude and in functional form, in the small $\omega\tau$ region and in the important range of $\omega\tau$ corresponding to the vicinity of the maxima in the relaxation rates.

The results for the continuum diffusion model are not shown in figure 1, but agree with the random walk results to within 0.7% for $g_{pp}(\omega\tau)$ over the range of $\omega\tau$ shown. The function $g_{-22}(\omega\tau)$ is related to the angular dependence of the spectral density functions on the azimuthal angle ϕ, as discussed in section 2, and it is zero for the continuum model but not for the random walk model.

The corresponding spectral density functions are shown for the case $z = a$ in figure 2 for the random walk and continuum models. The BPP results are not shown, but are the same as in figure 1 since they are independent of z. The magnitude of the BPP results are now comparable to the other models but the functional form is still quite different at small $\omega\tau$. The results for the random walk model show significant differences from those of the continuum model, unlike the case for $z = 10a$.

The general conclusions are therefore that the BPP model is unsatisfactory for these systems and that the continuum model is a good approximation for $g_{pp}(\omega\tau)$ for large z. This latter result is expected since the details of the lattice structure will become less important as z increases. Lattice diffusion models such as the random walk model are, however, necessary for small z and for calculating $g_{-22}(\omega\tau)$ since this is zero for a continuum model.

4.2. Single plane

For like-spin interactions between spins diffusing in the same plane ($z = 0$) the function $g_{11}(\omega\tau) = 0$ and the functions $g_{00}(\omega\tau)$, $g_{22}(\omega\tau)$ and $g_{-22}(\omega\tau)$ are shown in figures 3 and 4 for the BPP, random walk, mean field and continuum models. The BPP model is again an unsatisfactory approximation, especially in the small $\omega\tau$ limit, where it becomes constant. As shown in figure 3, all the other models show $\ln(1/\omega\tau)$ behaviour for $g_{00}(\omega\tau)$ in this limit, although their magnitudes can be significantly different from each other. The remaining independent $g_{pp'}(\omega\tau)$ do not diverge at $\omega\tau = 0$ but intersect the $\omega\tau = 0$ axis with finite slope, as shown in figure 4. In the case of $g_{22}(\omega\tau)$, which is linear in $\omega\tau$ in the low-frequency limit, this slope is non-zero for all but the BPP model. The slope of $g_{-22}(\omega\tau)$ at $\omega\tau = 0$ is zero.

These results show that the precise details of the diffusion model are quite important for $z = 0$, with the more rigorous mean field results showing appreciable differences to those for the random walk model and especially to those for the continuum model. The percentage difference between the spectral density functions for the random walk and mean

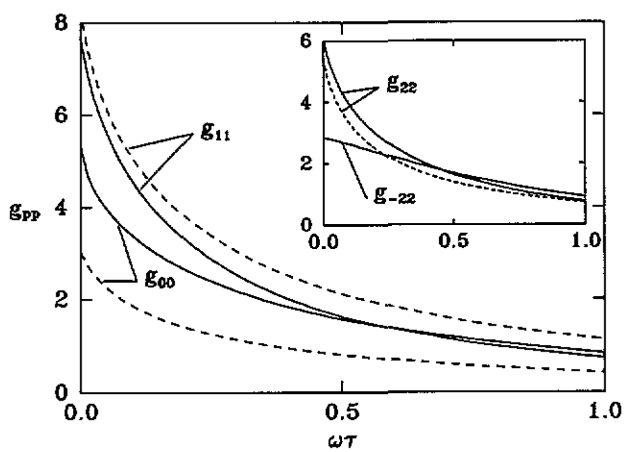

Figure 2. The functions $g_{pp'}(\omega\tau)$ for the random walk (——) and continuum (– – –) models for dipolar interactions between diffusing spins and fixed spins on square lattices separated by $z = a$. The function $g_{-22}(\omega\tau)$ is zero for the continuum model.

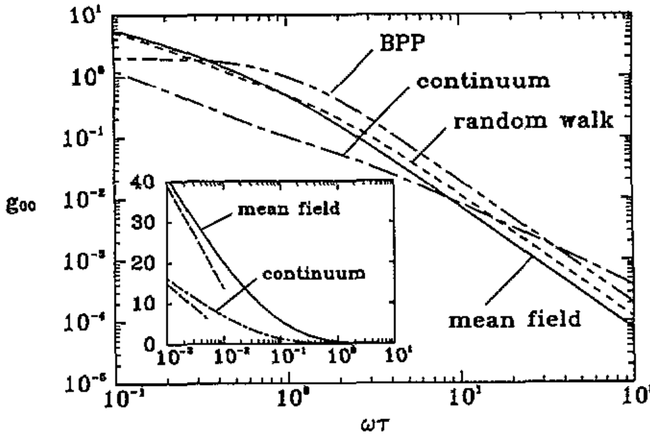

Figure 3. The function $g_{00}(\omega\tau)$ for the BPP, random walk, mean field and continuum models for interactions between spins diffusing on a square lattice ($z = 0$). The approach of the mean field and continuum models to the $\ln(1/\omega\tau)$ limit for small $\omega\tau$ is shown in the inset.

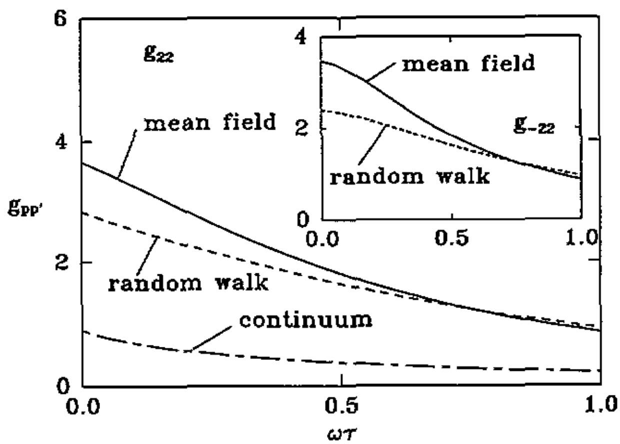

Figure 4. The functions $g_{22}(\omega\tau)$ and $g_{-22}(\omega\tau)$ for the same system as in figure 3.

field models becomes constant at both small and large $\omega\tau$. It is interesting to note that the numerical calculations are easier to compute to a given accuracy over a wide range of $\omega\tau$ for the more realistic mean field model than is the case for the continuum model.

Analytic approximations for the numerical results can be extremely useful (Sholl 1988) and the following functions have been found to fit the mean field results to good accuracy. The functions $g_{22}(\omega\tau)$ and $g_{-22}(\omega\tau)$ over the entire range of $\omega\tau$ and $g_{00}(\omega\tau)$ for $\omega\tau \geqslant 1.0$ may be approximated by

$$g_{pp'}(\omega\tau) \simeq \frac{S}{a + b(\omega\tau) + c(\omega\tau)^u + d(\omega\tau)^v + (\omega\tau)^2} \tag{30}$$

where the values of the parameters and the accuracy of the approximations are given in table 2.

Table 2. Parameters for the analytic approximations to the mean field spectral density functions.

	$g_{00}(\omega\tau)$	$g_{22}(\omega\tau)$	$g_{-22}(\omega\tau)$
S	0.7577	1.3858	1.3377
a	0.25	0.3791	0.3869
b	0.0	0.3905	0.0
c	0.4028	−0.1879	0.4210
d	−0.0632	0.0268	−0.2783
u	0.80	1.50	1.11
v	1.40	1.80	1.30
Maximum error	0.8%	1.1%	1.0%

A different functional form is required for $g_{00}(\omega\tau)$ for $\omega\tau < 1.0$, and the results can be described by

$$g_{00}(\omega\tau) \simeq -\frac{11.150\ln(29.81\omega\tau)}{\left[1 - 17.98(\omega\tau)^{0.87}\right]} \tag{31}$$

for $\omega\tau \leqslant 0.015$ accurate to within 0.6%. For $0.015 \leqslant \omega\tau \leqslant 2.5$

$$g_{00}(\omega\tau) \simeq -\frac{1}{\omega\tau}\sum_{n=0}^{5} \mathrm{A}_n x^n \tag{32}$$

where $x = \log_{10}(2\omega\tau)$ and is also accurate to within 0.6%, and where the coefficients A_n are

$$\mathrm{A}_0 = 0.2997 \qquad \mathrm{A}_1 = -0.1349 \qquad \mathrm{A}_2 = -0.2464$$
$$\mathrm{A}_3 = 0.0490 \qquad \mathrm{A}_4 = 0.1145 \qquad \mathrm{A}_5 = 0.0306.$$

The low-frequency limit of $-11.150\ln(29.81\omega\tau)$ for the mean field model may be compared with $-5.395\ln(62.55\omega\tau)$ for the continuum model. The appreciable difference between these forms is shown in the inset of figure 3. The low-frequency limits for the remaining independent spectral density functions for the mean field theory are $3.66 - 5\pi\omega\tau/2a^6S_{22}$ for $g_{22}(\omega\tau)$ and 3.46 for $g_{-22}(\omega\tau)$.

As for the case of $z > 0$, the BPP model is again unsatisfactory. The continuum model shows the correct functional form in the small-$\omega\tau$ limit, but the magnitude is significantly in error and again gives $g_{-22}(\omega\tau) = 0$. The lattice models are therefore necessary to give accurate results and also to give non-zero values of $g_{-22}(\omega\tau)$, and the mean field model is the most physically realistic of the models considered.

4.3. Relaxation rates

The longitudinal relaxation rates R_1 and $R_{1\rho}$ are linear combinations of spectral density functions and are given by equations (10) and (11). The relaxation rates are dimensionless functions of $\omega_0\tau$ and $\omega_1\tau$ when expressed in units of $4\pi Cc/15\omega_0 a^6$, and plots of the relaxation rates in these units are shown in figures 5 and 6 for the BPP and mean field models and various magnetic field orientations for like-spin interactions between spins diffusing on a square lattice ($z = 0$, $j = 0$, $\tau = \tau_c/2$) and for $\omega_1 = \omega_0/10^3$. If the mean time τ_c between jumps depended on the temperature T according to an Arrhenius relation, the relaxation

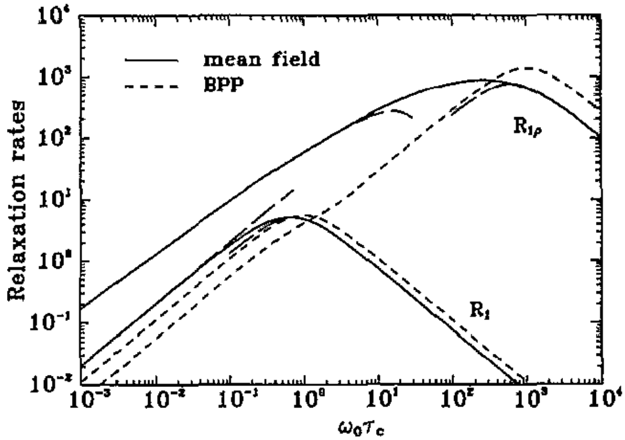

Figure 5. The relaxation rates R_1 and $R_{1\rho}$ as functions of $\omega_0\tau_c$ for interactions between spins diffusing on a square lattice. The results are for the magnetic field direction normal to the plane. The long-dash broken curves correspond to the low-frequency limits in section 4.2 and the high-frequency approximation of MacGillivray and Sholl (1985b).

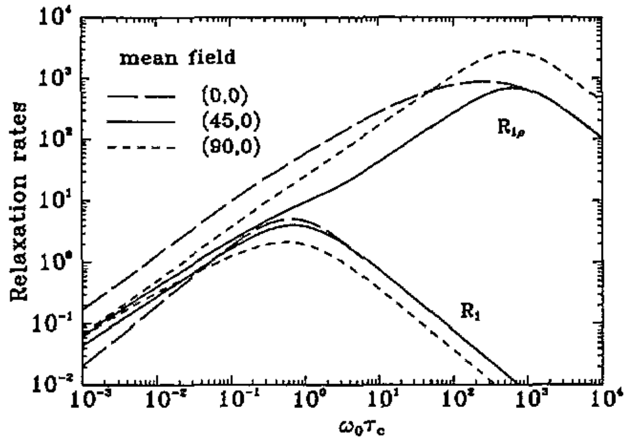

Figure 6. The mean field model results for some magnetic field directions different to those on figure 5.

rates plotted as functions of $\log(\omega\tau_c)$ would correspond to experimental relaxation rates plotted as functions of $1/T$.

Figure 5 shows the results for the BPP and mean field theories for the magnetic field direction oriented normal to the plane of spins. The form of the relaxation rates at large $\omega\tau$ (corresponding to high frequencies or low temperatures) is proportional to $(\omega\tau)^{-1}$, but there is a difference in magnitude between the models of 1.4 for R_1 and 2.6 for $R_{1\rho}$ in this limit. In the low-frequency (high-temperature) limit the BPP results are proportional to $\omega\tau$ for all magnetic field orientations, but this is true for the mean field model only for R_1 and if the magnetic field is normal to the plane of the spins, as in figure 5. This is because, in this case, R_1 depends only on $g_{\pm 22}(\omega\tau)$, which do not show logarithmic behaviour for small $\omega\tau$. In all other cases the relaxation rates are not proportional to $\omega\tau$ for small $\omega\tau$

because the relaxation rates then depend on $g_{00}(\omega\tau)$, which shows logarithmic behaviour in this limit.

The relaxation rates for the mean field theory are shown in figure 6 for three different orientations of the magnetic field direction. There are significant differences between the results for different field directions at all values of $\omega_0\tau_c$. The minimum and maximum values of the R_1 maximum for any field direction are 2.17 (in units of $4\pi Cc/15\omega_0 a^6$) at $\theta = 90°$, $\phi = 0°$ and 5.16 at $\theta = 0°$ respectively. The corresponding results for $R_{1\rho}$ are 123 at $\theta = 50°$, $\phi = 45°$ and 2770 at $\theta = 90°$, $\phi = 0°$.

The values of $\omega_0\tau_c$ and $\omega_1\tau_c$ at which the R_1 and $R_{1\rho}$ maxima occur are especially important parameters, since they can provide directly a value of τ_c at the temperature for which the maximum relaxation rate occurs. The values of $\omega_0\tau_c$ for which the R_1 maxima occur are given as a function of magnetic field orientation for the BPP and mean field theories in figure 7 for the range of angles sufficient to specify the results for any orientation. It can be seen that the variation with θ, ϕ is similar for the two models, but that the magnitudes are different. The comparable results for the mean field theory are given in figure 8 for the $R_{1\rho}$ maximum. The corresponding BPP results are not shown, but vary by only 0.02% over the entire range of θ and ϕ and the value is 1.0. Also shown in figures 7 and 8 are the results for a circular average about the direction normal to the plane. The anisotropy of the position of the maxima is therefore quite different between the models for $R_{1\rho}$ compared with R_1. These results again show the inadequacy of the BPP model for two-dimensional systems.

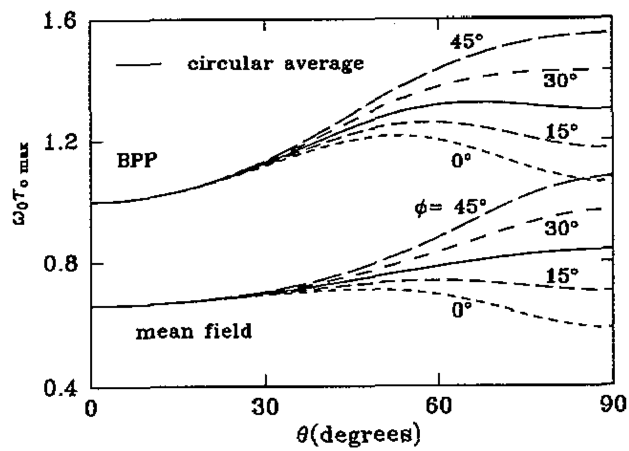

Figure 7. The values of $\omega_0\tau_c$ at which the maxima of R_1 occur as functions of the angles θ, ϕ of the magnetic field direction relative to the crystal axis.

5. Discussion

The functional form of the dependence of the spectral density functions as a function of the orientation of the magnetic field direction relative to the crystal axes has been obtained for dipole interactions between spins undergoing discrete lattice diffusion on separate parallel planes and for interactions between spins diffusing in a plane. The details of the reciprocal space formulation for evaluating the spectral density functions for two-dimensional lattice

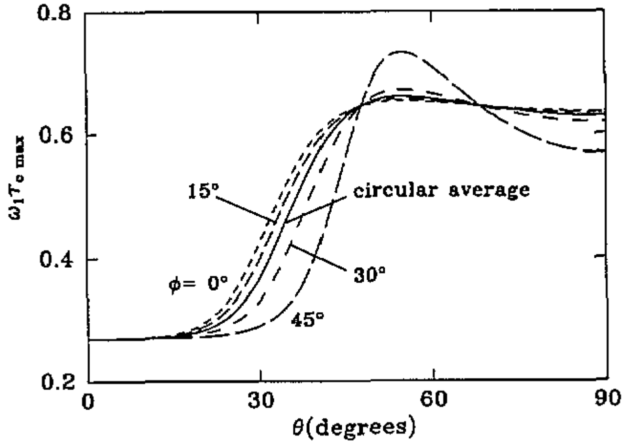

Figure 8. The values of $\omega_1\tau_c$ at which the maxima of $R_{1\rho}$ occur as functions of the magnetic field direction.

diffusion have been developed and applied to the random walk and mean field models for diffusion on a square lattice.

The results from the random walk and mean field models have been compared with the results from the BPP and continuum models. The BPP model is quite unsuitable for two-dimensional diffusion since it gives the incorrect functional form for the relaxation rates in the low-frequency (high-temperature) limit and can also give significant differences in the magnitudes of the spectral density functions and relaxation rates from the more detailed lattice diffusion models. The continuum model is quite satisfactory, as would be expected physically, for interactions between well separated planes, but is less accurate for interactions between spins diffusing in a single plane. The lattice diffusion models are also necessary to calculate the dependence of the spectral density functions on the azimuthal angle between the magnetic field direction and the normal to the plane.

In the case of interactions in a single plane, the mean field model is exact in the limit of low spin concentrations and an accurate analytic approximation has been obtained for the spectral density functions for diffusion on a square lattice. These results should also be a good approximation for other spin concentrations that are not too large. The mean field model is a reasonable approximation for three-dimensional systems unless the spin concentration approaches unity (Faux *et al* 1986). The range of spin concentrations over which the mean field model is valid might, however, be less for two-dimensional diffusion since the three-dimensional encounter model for high spin concentrations is not valid for two-dimensional diffusion.

While the functional form of the spectral density functions and relaxation rates in the high-frequency limit is similar for lattice diffusion models in one, two or three dimensions, this is not the case for the low-frequency limit. For example, anisotropic diffusion models in three-dimensional hexagonal crystals (Sholl 1987) showed significant differences between the results for one-, two- and three-dimensional diffusion. The spectral density functions for interactions in a plane show the $\ln(1/\omega\tau)$ behaviour as $\omega\tau \to 0$, but this limit is only approached for values of $\omega\tau$ corresponding to relaxation rates well below the maximum rate and might therefore be difficult to observe experimentally.

The relaxation rates for two-dimensional diffusion show a much stronger dependence on magnetic field direction than is the case for three-dimensional cubic systems. An interesting consequence of this dependence on magnetic field direction is that the magnetization recoveries show non-exponential behaviour at long times for polycrystalline samples (Barton and Sholl 1976). The stronger dependence on the field direction in two-dimensional systems would mean that the non-exponential magnetization recoveries would be observed at shorter times.

The general analysis of two-dimensional systems developed above can be easily extended to other lattices and other like- and unlike-spin planar systems.

Appendix. Transformation of $T_p(q, j, z)$

The function $T_p(\boldsymbol{q}, \boldsymbol{j}, z)$ is defined by

$$T_p(\boldsymbol{q}, \boldsymbol{j}, z) = \sum_{l} \frac{Y_{2p}(\Omega_\alpha)}{r_\alpha^3} \exp(\mathrm{i}\boldsymbol{q} \cdot \boldsymbol{r}_\alpha) \tag{A1}$$

where $\boldsymbol{r}_\alpha$ are the vectors $\boldsymbol{l} + \boldsymbol{j} + z\hat{\boldsymbol{k}}$. In terms of basis vectors $\boldsymbol{a}_1$, $\boldsymbol{a}_2$ where $|\boldsymbol{a}_1| = a$, and two-dimensional reciprocal lattice vectors $\boldsymbol{b}_1$, $\boldsymbol{b}_2$ defined by $\boldsymbol{a}_i \cdot \boldsymbol{b}_j = a\delta_{ij}$, the vectors $\boldsymbol{r}_\alpha$ and $\boldsymbol{q}$ are

$$\boldsymbol{r}_\alpha = z\hat{\boldsymbol{k}} + \boldsymbol{j} + \boldsymbol{l} = z\hat{\boldsymbol{k}} + (j_1\boldsymbol{a}_1 + j_2\boldsymbol{a}_2) + (\lambda_1\boldsymbol{a}_1 + \lambda_2\boldsymbol{a}_2) \tag{A2}$$

$$\boldsymbol{q} = (q_1\boldsymbol{b}_1 + q_2\boldsymbol{b}_2). \tag{A3}$$

The summation over $\boldsymbol{l}$ in (A1) then corresponds to λ_1 and λ_2 summed over integers from $-\infty$ to ∞. This two-dimensional sum can be transformed into a sum over two-dimensional reciprocal lattice coordinates μ_1, μ_2 by using the Poisson summation formula in a similar way to the case $\boldsymbol{q} = 0$ considered by Sholl (1966). For $p \geqslant 0$ the result is

$$T_p(\boldsymbol{q}, \boldsymbol{j}, z) = A_p \sum_{\mu_1,\mu_2=-\infty}^{\infty} F_p(\mu_1, \mu_2, j_1, j_2) f_{\mu_1,\mu_2} \exp[-2\pi(z/a) f_{\mu_1,\mu_2}] \tag{A4}$$

where

$$A_p = \frac{4\pi^2(-\mathrm{i})^p}{a|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\left(\frac{5}{4\pi(2-p)!(2+p)!}\right)^{1/2}$$

$$F_p(\mu_1, \mu_2, j_1, j_2) = \exp\{\mathrm{i}[p\omega_{\mu_1,\mu_2} - 2\pi(j_1\mu_1 + j_2\mu_2)]\}$$

$$f_{\mu_1,\mu_2} = |(\mu_1 + a\rho_1)\boldsymbol{b}_1 + (\mu_2 + a\rho_2)\boldsymbol{b}_2|$$

$$\tan\omega_{\mu_1,\mu_2} = \frac{[-a_{2x}(\mu_1 + a\rho_1) + (\mu_2 + a\rho_2)]}{(\mu_1 + a\rho_1)a_{2y}}$$

where $a_{2x} = \boldsymbol{a}_1 \cdot \boldsymbol{a}_2/a^2$, $a_{2y} = \sqrt{1 - a_{2x}^2}$ and $\boldsymbol{q} = 2\pi\boldsymbol{\rho}$. The values of $T_p(\boldsymbol{q}, \boldsymbol{j}, z)$ for $p < 0$ can be obtained from

$$T_{-p}(\boldsymbol{q}, \boldsymbol{j}, z) = (-1)^p T_p^*(-\boldsymbol{q}, \boldsymbol{j}, z). \tag{A5}$$

The expression (A4) is not valid for $z = 0$. In this case the transformation can be made to a rapidly converging form by using an auxiliary function (Nijboer and DeWette 1957). The results are

$$T_0(\boldsymbol{q}, \boldsymbol{j}, 0) = \frac{-\sqrt{5}}{2\pi a^3}\left(\sum_{\lambda_1,\lambda_2}{}' \frac{\exp(\mathrm{i}\boldsymbol{q}\cdot\boldsymbol{\sigma}_{\lambda j})}{\sigma_{\lambda j}^3}\Gamma(\tfrac{3}{2}, \pi\sigma_{\lambda j}^2) - \tfrac{2}{3}\pi^{3/2}\delta_{\boldsymbol{j},0} + \frac{\pi^2 a^2}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\sum_{\mu_1,\mu_2} F_0(\mu_1, \mu_2, j_1, j_2) f_{\mu_1,\mu_2}\Gamma(-\tfrac{1}{2}, \pi f_{\mu_1,\mu_2}^2)\right) \tag{A6}$$

$$T_1(\boldsymbol{q}, \boldsymbol{j}, 0) = 0 \tag{A7}$$

$$T_2(\boldsymbol{q}, \boldsymbol{j}, 0) = \frac{\sqrt{5}}{\sqrt{6}\pi a^3}\left(\sum_{\lambda_1,\lambda_2}{}' \frac{\exp[\mathrm{i}(2\phi_{\lambda j} + \boldsymbol{q}\cdot\boldsymbol{\sigma}_{\lambda j})]}{\sigma_{\lambda j}^3}\Gamma(\tfrac{5}{2}, \pi\sigma_{\lambda j}^2) - \frac{\pi^2 a^2}{|\boldsymbol{a}_1 \times \boldsymbol{a}_2|}\sum_{\mu_1,\mu_2}{}' F_2(\mu_1, \mu_2, j_1, j_2) f_{\mu_1,\mu_2}\Gamma(\tfrac{1}{2}, \pi f_{\mu_1,\mu_2}^2)\right) \tag{A8}$$

where the prime on the summation over λ_1, λ_2 denotes the exclusion of the $\lambda_1 = \lambda_2 = 0$ term when $\boldsymbol{j} = 0$, and the prime on the summation over μ_1, μ_2 denotes the exclusion of the $\mu_1 = \mu_2 = 0$ term if $\boldsymbol{q} = 0$, and where $\boldsymbol{\sigma}_{\lambda j}$ is the projection of the vector $\boldsymbol{r}_\alpha$ onto the xy plane; i.e. $\boldsymbol{\sigma}_{\lambda j} = \boldsymbol{r}_\alpha - z\hat{\boldsymbol{k}} = \boldsymbol{l} + \boldsymbol{j}$. The term $\Gamma(x, \pi\sigma^2)$ is the incomplete gamma function.

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