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Correlation functions for simple hopping in a simple cubic lattice

Peter A. Fedders and O. F. Sankey
Department of Physics, Washington University, St. Louis, Missouri 63130

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We calculate the correlation functions for a single specific particle and for a pair of specific particles in an ensemble of particles making nearest-neighbor simple jumps in a simple cubic lattice. These correlation functions can be used to obtain tracer correlation factors and NMR relaxation times due to motionally altered I-S (unlike spin) or I-I (like spin) dipolar interactions. In particular we calculate T_1 due to the I-I dipolar interaction for various concentrations of particles as may be appropriate for some metal hydrides at different concentrations. Our results show that the T_1 calculated using the random-walk model is in error by more than 15% at low concentrations and by almost 100% at high concentrations.

I. INTRODUCTION

Starting with Bloembergen, Purcell, and Pound[1] (BPP), an enormous amount has been published on correlation functions for atomic motion and nuclear-magnetic-resonance (NMR) relaxation rates due to motionally altered dipolar interactions. One significant improvement on the simple BPP or single-relaxation-time model is the random-walk model first used by Torrey[2] which takes into account some of the correlations introduced by specific lattices. Although the random-walk model predicts significant departures from the single-relaxation-time model, the single-relaxation-time model is still used sometimes for quantitative analysis. Further, Wolf[3] has recently introduced a model of monovacancy hopping which is valid when the concentration of vacancies in a lattice approaches zero. Under some conditions the T_1 predicted by the monovacancy-hopping model shows that the single-relaxation-time model can lead to errors of more than 300% and that random-walk model can lead to errors of more than 100%. However, in spite of these rather large discrepancies at high and low temperatures, all of these models predict almost the same value for T_1 at the T_1 minimum when the relaxation is due to $I-I$ (like spin) dipolar interactions.

Recently[4] we have developed a formalism which, at least in principle, allows one to calculate all correlation functions and thus all relevant relaxation rates for any simple-hopping system. In this paper we apply this formalism to calculating the correlation functions for one specific particle and for a pair of specific particles hopping via nearest-neighbor jumps in a simple-cubic lattice with an arbitrary concentration of occupied sites. We find that the random-walk model and the single-relaxation-time model yield T_1's due to I-I dipolar interactions that can be in error by as much as 100% and 300%, respectively, at high concentrations and by 18% and 230%, respectively, at low concentrations. Oddly enough, the value of T_1 (but not its position) at the T_1 minimum does not depend on whether or not a correct theory is used. The tracer correlation factors obtained with our theory at various concentrations are virtually identical to those obtained by computer simulations. As the concentration of particles approaches one, our results agree with Wolf's. For concentrations of particles between zero and one, our results will allow a meaningful quantitative comparison between different experiments on some metal hydrides. Further, the techniques developed in this paper will be useful in calculating similar results for the fcc lattice and for the octahedral and tetrahedral interstitial sites in a bcc lattice. These lattices are believed to describe the occupied sites in many metal hydrides.

In the remainder of this section we shall discuss a number of details which are necessary for an understanding of the problem. This includes a clarification of the "simple-hopping model," which is the model we use. Further, we discuss the dynamical variables involved and the correlation functions that are relevant to T_1 calculations. In Sec. II we obtain expressions for T_1 in terms of the relevant correlation functions and briefly review the physics and results of models which previous investigators have proposed. The results of our calculations are presented, discussed, and compared with previous theories and existing experimental data in Sec. III. Our calculations refer to two distinct approximations. The first of these is the mean-field approximation which has a very limited range of validity and the second is a much better approximation which we call the multiple-scattering approximation. The details of our calculations for the single-specific-particle correlation function and for the correlation function for a pair of specific particles are contained in Secs. IV and V, respectively. Sections IV and V depend heavily on previous work and might be considered as appendixes. We believe that the results of Secs. I–III can be understood without reading Secs. IV and V.

In what follows we shall use greek letters to denote lattice sites that a hopping particle can occupy. In the simple-hopping problem one assumes that the probability per unit time that a particle at the site α will hop to a nearby vacant site β is given by the hopping rate $\Gamma_{\alpha\beta}$ and that this process depends neither on the time nor on the occupancy of sites other than α and β. However, a particle can never hop to a site that is already occupied by another particle. This is the model that most authors use when refering to hopping or atomic migration. We note that such a simple-hopping procedure does not necessarily obtain. For example, the effective potential well at a given site could depend on the occupancy of a number of sites near the given site. In this case the probability per unit time for a particle to hop from site α to site β would depend on the occupancy of a number of sites near the sites α and β. Other types of complications could also occur such as the hopping rate depending on the length of time that a particle has already spent at a site. However, in the remainder of this paper, we shall ignore the possibility of such complications.

As discussed in Ref. 4, there are two types of stochastic variables that are of interest in the hopping problem. One type of variable called n_α denotes the occupancy of the site α by any particle. Thus $n_\alpha = 1$ if the site is occupied (by any particle) and $n_\alpha = 0$ if the site α is vacant. The other type of variable called $p_{i\alpha}$ denotes the occupancy of the site α by the specific (distinguishable) particle labeled i. Thus $p_{i\alpha} = 1$ if the specific particle i is at the site α and $p_{i\alpha} = 0$ otherwise.

Correlation functions containing the n_α variables can be measured by neutron scattering and can contribute to NMR relaxation rates due to quadrupolar processes. Here, however, we consider only those correlation functions relevant to dipolar relaxation. Further, at this point, we also specialize to Bravais lattices where all sites are equivalent. One of the two correlation functions which we consider is the two-point distinguishable particle correlation function defined as

$$D_i(\vec{R}_\alpha - \vec{R}_\beta, t) = \langle \rho_{i\alpha}(t)\rho_{i\beta}(0)\rangle\,\Theta(t)\,, \tag{1}$$

$$\rho_{i\alpha} = N^{1/2} p_{i\alpha}\,. \tag{2}$$

In this equation N is the number of sites in the lattice, Θ is the step function, the brackets $\langle x\rangle$ denote the ensemble average of x, and $\vec{R}_\alpha$ is the lattice position of the site α. The quantity D_i in Eq. (1) is proportional to the probability that the particle i is at the site β at time zero and at the site α at a later time t. Thus it describes the motion of a single particle with respect to the lattice and can be used to calculate relaxation rates due to the I-S dipolar interaction between a hopping spin and other stationary spins.

The other function which we consider is the four-point, two-time distinguishable particle correlation function defined as

$$D_{ij}(\vec{R}_\alpha, \vec{R}_{\bar\alpha}; \vec{R}_\beta, \vec{R}_{\bar\beta}; t) = \langle \rho_{i\alpha}(t)\rho_{j\bar\alpha}(t)\rho_{i\beta}(0)\rho_{j\bar\beta}(0)\rangle\Theta(t)\,, \tag{3}$$

where i and j refer to two different specific particles. This function is proportional to the probability that particles i and j are at the sites β and $\bar\beta$, respectively, at time zero and are at the sites α and $\bar\alpha$, respectively, at time t. Actually, the function in Eq. (3) yields more information than we need and thus we define

$$\tilde{D}_{ij}(\vec{R}_\alpha, \vec{R}_\beta, t) = N^{-2}\sum_{\gamma\bar\gamma} D_{ij}(\vec{R}_\alpha + \vec{R}_\gamma, \vec{R}_\gamma; \vec{R}_\beta + \vec{R}_{\bar\gamma}, \vec{R}_{\bar\gamma}; t)\,. \tag{4}$$

This function is proportional to the probability that the particles i and j are separated by $\vec{R}_\beta$ at time zero and by $\vec{R}_\alpha$ at time t. This is the function desired for calculating relaxation rates due to the I-I dipolar interaction between pairs of hopping spins.

II. EXPRESSIONS FOR T_1

In what follows we shall let c denote the concentration of particles (the number of particles divided by the number of sites) and let $\bar{c}$ denote the concentration of vacancies so that

$$\bar{c} = 1 - c\,. \tag{5}$$

Further, it is convenient to Fourier transform all quantities in space and time. All quantities $A(t)$ depending on a single time difference are transformed as

$$A(\omega) = \int_{-\infty}^{\infty} dt\, A(t)\, e^{i\omega t}\,. \tag{6}$$

Quantities $A(\vec{R}_\alpha)$ depending on a single-space coordinate [like D_i in Eq. (1)] are transformed as

$$A(\vec{q}) = \sum_\alpha A(\vec{R}_\alpha)\, e^{-i\vec{q}\cdot\vec{R}_\alpha}\,, \tag{7}$$

while quantities $A(\vec{R}_\alpha, \vec{R}_\beta)$ depending on two distinct space coordinates [like $\tilde{D}_{ij}$ in Eq. (4)] are transformed as

$$A(\vec{q}, \vec{q}\,') = \sum_{\alpha,\beta} A(\vec{R}_\alpha, \vec{R}_\beta)\exp(-i\vec{q}\cdot\vec{R}_\alpha + i\vec{q}\,'\cdot\vec{R}_\beta)\,, \tag{8}$$

where $\vec{q}$ is a wave vector in the first Brillouin zone. For a Bravais lattice we have that

$$\Gamma_{\alpha\beta} = \Gamma_0 f(\vec{R}_\alpha - \vec{R}_\beta)\,, \tag{9}$$

where $f(\vec{R}_\alpha) = 1$ if $\vec{R}_\alpha$ is a nearest neighbor to the origin and it equals zero otherwise. Thus Γ_0 is the hopping rate for a particle to hop to a single vacant nearest neighbor. The Fourier transform of $\Gamma_{\alpha\beta}$ is $\Gamma(\vec{q})$ and [by Eq. (7)] for the sc lattice we have

$$\Gamma(\vec{q}) = \Gamma_0 f(\vec{q})\,,\quad f(\vec{q}) = 2\sum_i \cos q_i a\,, \tag{10}$$

where a is a cube edge and latin subscripts denote the three Cartesian directions.

The relationship between various relaxation rates and the correlation functions D_i and $\tilde{D}_{ij}$ are described in many places.[5] Although we shall present results for both D_i and $\tilde{D}_{ij}$ in this section, we shall compute only T_1 due to the I-I dipolar interaction between pairs of hopping spins. By taking advantage of the cubic symmetry of the sc lattice, one can write T_1 due to this process as[6]

$$\begin{aligned} T_1^{-1} = (\tfrac{1}{20}A)\,[&\tilde{D}'_{00}(\omega)(2-5h) + \tilde{D}'_{00}(2\omega)(8-20h) \\ &+ \tilde{D}'_{11}(\omega)(24+90h) + \tilde{D}'_{11}(2\omega)(96-240h) \\ &+ \tilde{D}'_{22}(\omega)(6-15h) + \tilde{D}'_{22}(2\omega)(24+90h)]\,, \end{aligned} \tag{11}$$

where

$$A = \frac{I(I+1)\hbar^2\gamma^4 c}{a^6}\,,\quad h = \sum_i l_i^4 - \frac{3}{5}\,,$$

where γ is the gyromagnetic moment of the spin I, ω is the frequency of the experiment, the l_i are the direction cosines of the external magnetic field with respect to the cubic axes, and the angular average of h vanishes. Further,

$$\tilde{D}'_{\alpha\alpha}(\omega) = N^{-2}\sum_{\vec{q},\vec{q}'} T_\alpha(\vec{q})\tilde{D}'_{ij}(\vec{q},\vec{q}',\omega)\,T^*_\alpha(\vec{q}')\,, \tag{12}$$

where $\tilde{D}'$ denotes the real part of $\tilde{D}$ and the $T_\alpha(\vec{q})$ are given by

$$\begin{aligned} T_0(\vec{q}) &= T_{xx}(\vec{q}) + T_{yy}(\vec{q}) - 2T_{zz}(\vec{q})\,, \\ T_1(\vec{q}) &= T_{xz}(\vec{q}) - iT_{yz}(\vec{q})\,, \\ T_2(\vec{q}) &= T_{xx}(\vec{q}) - T_{yy}(\vec{q}) - 2iT_{xy}(\vec{q})\,, \end{aligned} \tag{13}$$

where the $T_{ij}(\vec{q})$ are the Fourier transforms of

$$T_{ij}(\vec{R}) = \begin{matrix} a^3 R_i R_j / R^5\,, & \vec{R} \neq 0 \\ 0\quad\,, & \vec{R} = 0 \end{matrix} \tag{14}$$

where R_i is the ith Cartesian component of $\vec{R}$.

Given the correlation function $\tilde{D}_{ij}(\vec{q},\vec{q}',\omega)$, the summations in Eq. (12) are performed numerically. The functions $T_{ij}(\vec{q})$ are easily computed using Ewald's method[7] and one can express the results as

$$T_1^{-1} = (A/\omega)\,[g_0(\omega\tau_c) + hg_1(\omega\tau_c)]\,, \tag{15}$$

where we have defined a correlation time τ_c and a correlation rate Γ_c as

$$\Gamma_c = 1/\tau_c = 6\bar{c}\,\Gamma_0\,. \tag{16}$$

The factor of 6 obtains because there are six nearest neighbors in an sc lattice and the factor of $\bar{c}$ because the probability of an arbitrary site being vacant is $\bar{c}$.

Expressions similar to Eq. (11) can be readily derived for relaxation due to the I-S dipolar interaction and also for other relaxation rates such as T_2 or $T_{1\rho}$. The heart of all of these problems is the calculation $\tilde{D}_{ij}$ and D_i. Since all of the numerical summations are rather easily performed on computers, we shall not display results for all values of $\omega\tau_c$ except in the case of the multiple-scattering approximation with $c = 0.85$. (However, tables of T_1 vs $\omega\tau_c$ for any concentration are available from the author upon request.) Instead we shall display the results at high and low frequencies in terms of the dimensionless constants $b_\alpha(\infty)$ and $b_\alpha(0)$ defined by the equations

$$\begin{aligned} g_\alpha(x) &\to b_\alpha(\infty)/x\,,\quad x \gg 1 \\ g_\alpha(x) &\to x\,b_\alpha(0)\,,\quad x \ll 1\,, \end{aligned} \tag{17}$$

where $\alpha = 0$ or 1. The b's for various models and concentrations are displayed in Table I. The

TABLE I. Dimensionless constants $b_0(0)$, $b_0(\infty)$, and $b_1(\infty)$ defined by Eq. (17) for the various theories discussed in the text. The abbreviations SRT, RW, MV, MF, and MS are used, respectively, for the single-relaxation-time model, the random-walk model, the monovacancy model, the mean-field approximation, and the multiple-scattering approximation. The MV theory applies only in the limit as $c \to 1$ while the b's for the SRT, RW, and MF theories do not depend explicitly on c. The quantity $b_1(0)$ is zero for all of the theories. All of the b's were computed from the equations in this paper except for those for the MV theory which were taken from Wolf's (Ref. 3). The values obtained for the RW model agree with the work of previous investigators (Refs. 3 and 8).

Theory	$b_0(0)$	$b_0(\infty)$	$b_1(\infty)$
SRT (any c)	8.40	13.44	−8.30
RW (any c)	17.91	10.36	−7.17
MV ($c \to 1$)	28.53	4.57	−3.09
MF (any c)	19.87	8.76	−5.67
MS ($c = 0.20$)	20.29	8.76	−5.67
MS ($c = 0.40$)	21.35	8.76	−5.67
MS ($c = 0.60$)	22.84	8.76	−5.67
MS ($c = 0.80$)	25.17	8.76	−5.67
MS ($c = 0.90$)	27.00	8.76	−5.67
MS ($c \to 1$)	30.86	4.37	−3.00

monovacancy model is valid only for $\bar{c} \ll 1$ while the $g_\alpha(x)$ are independent of c for the single-relaxation-time model, the random-walk model, and the mean-field approximation. However, the $g_\alpha(x)$ depend upon c explicitly in the multiple-scattering approximation. The error in our numerical computations are less than 1%.

We shall now give a very brief summary of the results of some of the currently used models. In the simple BPP or single-relaxation-time model[1] one assumes that the correlation function can be described by a single rate. Thus the two relevant correlation functions are

$$D_i(\vec{q}, \omega) = 1/(-i\omega + \Gamma_c)\,, \tag{18a}$$

$$\tilde{D}_{ij}(\vec{q}, \vec{q}'; \omega) = N\delta(\vec{q} - \vec{q}')/(-i\omega + 2\Gamma_c)\,. \tag{18b}$$

These correlation functions do not exhibit a diffusive character at long wavelengths and, when Fourier transformed to configuration space, are proportional to δ functions in $\vec{R}$.

In the random-walk approximation[2] one assumes that any specific particle moves through the lattice in the same way that a single particle would move through an otherwise empty lattice. In more sophisticated versions of this model blocking due to occupied sites is taken into account by assuming that the correlation time is given by Eq. (16). The relevant correlation functions are given by the equations

$$D_i(\vec{q}, \omega) = 1/[-i\omega + \omega_c(\vec{q})], \tag{19a}$$

$$\tilde{D}_{ij}(\vec{q}, \vec{q}', \omega) = N\delta(\vec{q} - \vec{q}')/[-i\omega + 2\omega_c(\vec{q})]\,, \tag{19b}$$

where

$$\omega_c(\vec{q}) = \Gamma_c[1 - \tfrac{1}{6}f(\vec{q})]\,. \tag{20}$$

As can be seen easily, Eq. (19a) predicts a diffusive behavior at long wavelengths with a diffusion coefficient D given by

$$D = \bar{c}\,\Gamma_0 a^2 = \tfrac{1}{6}\,\Gamma_c a^2\,. \tag{21}$$

Torrey's original calculations with this model included a number of additional approximations in order to make the numerical integrations easier. More recently more precise numerical calculations for the sc lattice have been made by Wolf[3] and Sholl.[8] As can be seen from Table I, the random-walk model yields corrections to the single-relaxation-time model that are of the order of a factor of 2.

Recently Wolf[3] has made calculations of T_1 from a monovacancy model. This model is the simple-hopping model applied in the limit where there is only one vacancy in an infinite crystal and thus it is applicable only in the limit where $c \to 1$ (or $\bar{c} \to 0$). This limit is an excellent approximation for normal crystals where typical vacancy concentrations due to thermal disorder are less than 10^{-3}. Since the calculations consist essentially of computing all rearrangements of pairs of atoms due to an encounter with a single vacancy, these results should be exact to within the limits of the numerical computations. Although Wolf's results in general cannot be easily expressed analytically, the limiting cases are included in Table I. As can easily be seen, his results show that the random walk theory is in error by more than 100% when $c \to 1$ and that the single-relaxation-time model is even worse.

III. RESULTS AND DISCUSSION

As mentioned in Sec. I, we have recently developed a formalism which allows one, in principle, to calculate any correlation function using the simple-hopping model. In this paper we wish to examine two distinct approximations using our formalism. The simplest (and least accurate) of these approximations is the mean-field approximation which is a well-defined, consistent approximation both physically and mathematically. Physically the approximation consists of assuming that any site that a single specific particle might hop to has a probability $\bar{c}$ of being vacant. Further, when considering a pair of specific particles, one assumes that each particle travels in its own mean field but with the additional restriction that the two particles cannot occupy the same lattice site.

Using our formalism the mean-field approximation for $D_i(\vec{q}, \omega)$ and $\tilde{D}_{ij}(\vec{q}, \vec{q}', \omega)$ are both easily obtained. The details of these approximations are discussed in Secs. IV and V and we present only the results here. The mean-field approximation for $D_i(\vec{q}, \omega)$ is identical with the expression given by Eq. (19a) and thus the diffusion coefficient D is given by Eq. (21). However, the mean-field approximation for $\tilde{D}_{ij}(\vec{q}, \vec{q}', \omega)$ is not identical to Eq. (19b). Instead it is effectively[9] given by the expression

$$\tilde{D}_{ij}(\vec{q}, \vec{q}', \omega) = d_0(\vec{q}, \omega)\,N\delta(\vec{q} - \vec{q}') + \frac{\frac{2}{3}\Gamma_c\, d_0(\vec{q}, \omega)\, d_0(\vec{q}', \omega)\left(\sum_i \cos q_i a \cos q_i' a\right)}{B(\omega)}\,, \tag{22}$$

where

$$d_0(\vec{q}, \omega) = [-i\omega + 2\omega_c(\vec{q})]^{-1}\,, \tag{23a}$$

$$B(\omega) = 1 - \frac{2}{3}\,\Gamma_c\, N^{-1} \sum_{\vec{q}} (\cos^2 q_x a - \cos q_x a \cos q_y a)\, d_0(\vec{q}, \omega)\,. \tag{23b}$$

The first term in Eq. (22) is the random-walk model result while the second term is a correction to the random-walk model that arises because the two particles i and j cannot occupy the same site. As can be seen from Table I, this restriction lowers T_1 by 11% at low frequencies and raises T_1 by 18% at high frequencies. As one would expect, the mean-field approximation becomes exact as c approaches zero or ω approaches infinity. Thus the random-walk model is wrong even in these relatively trivial limits.

It is easily seen where the mean-field approximation goes wrong. For example, suppose that a specific particle has just hopped from site a to site b. The mean-field approximation now says that site a has a probability $\bar{c}$ of being vacant when, in fact, site a is surely vacant because the specific particle has just hopped out of it. In Sec. III we discuss the multiple-scattering approximation to $D_i(\vec{q}, \omega)$ which is much better than the mean-field approximation. An exact definition and discussion of the approximation is given in Sec. III. Here we only note that the approximation is exact when $c \to 0$ or $c \to 1$ and that we believe it to be exact to about 1% at intermediate concentrations. The diffusion coefficient obtained in this approximation is

$$D = \tfrac{1}{6} f_t \Gamma_c a^2 , \tag{24}$$

where f_t is the correlation factor[10, 11] or tracer correlation factor. From the multiple-scattering approximation described in Sec. IV we obtain the expression

$$\begin{aligned} f_t &= (1 - 2\alpha)/[1 + (6c - 4)\alpha/(2 - c)] , \\ \alpha &\cong 0.1059 . \end{aligned} \tag{25}$$

This function agrees with values of f_t obtained from the computer simulations of De Bruin and Murch[12] to within the accuracy that one can read their figure (~1%).

The exact values of $D_i(\vec{q}, \omega)$ in the multiple-scattering approximation can be calculated at each value of $(\vec{q}, \omega)$ using Eqs. (31), (32), and (37)–(42) from Sec. IV. As a partial simplification we have noted that as a purely numerical approximation one can express D_i as

$$D_i(\vec{q}, \omega) = [-i\omega + \bar{K}(\vec{q}, \omega)]^{-1} , \tag{26a}$$

$$\bar{K}(\vec{q}, \omega) = \omega_c(\vec{q})\{1 - p_1/[p_2(\vec{q}) - i\omega]\} , \tag{26b}$$

where $\omega_c(\vec{q})$ is given by Eq. (20) and p_1 and $p_2(\vec{q})$ are given by the prescription contained in Eq. (44) in Sec. III. This numerical approximation preserves the spectral integral of $D_i(\vec{q}, \omega)$, is exact at $c = 0$ or $c = 1$, and is in error by no more than 3% at intermediate concentrations for any value of $(\vec{q}, \omega)$. Using Eqs. (26) can result in an enormous savings of computer time since $\omega_c(\vec{q})$, p_1, and $p_2(\vec{q})$ are independent of ω.

The multiple-scattering approximation for $\tilde{D}_{ij}(\vec{q}, \vec{q}\,', \omega)$ is discussed in Sec. IV. The expression obtained is effectively[9]

$$\begin{aligned} \tilde{D}_{ij}(\vec{q}, \vec{q}\,', \omega) = {} & N\delta(\vec{q} - \vec{q}\,')\, d_1(\vec{q}, \omega) + \tfrac{2}{3}\Gamma_c d_0(\vec{q}, \omega) \\ & \times d_0(\vec{q}\,', \omega) \sum_i \cos q_i a \cos q_i' a \;, \end{aligned} \tag{27}$$

where $d_0(\vec{q}, \omega)$ is given by Eq. (23a),

$$d_1(\vec{q}, \omega) = \int_{-\infty}^{\infty} \frac{d\bar{\omega}}{2\pi}\, D_i(\vec{q}, \omega) D_i(\vec{q}, \omega - \omega) , \tag{28}$$

and $D_i(\vec{q}, \omega)$ is the function discussed in the previous paragraph. As discussed in Sec. V, to the best of our knowledge Eq. (27) is exact to between 4% and 8% when $c = 1$, is better than 4% if $c < 0.9$, and approaches 2% accuracy as $c \to 0$. These estimates are discussed further at the end of Sec. V.

The results of our T_1 computations in the asymptotic regions at a variety of concentrations are included in Table I. As mentioned earlier, all of the models and approximations listed yield virtually identical values of T_{1m} (the value of T_1 at the T_1 minimum). We find this observation somewhat surprising in view of the large variations in the asymptotic regions and we have no explanation for it. The value of $\omega\tau_c$ for which $T_1 = T_{1m}$ varies by a factor of 2 over the range of theories. However, because the T_1 minimum is rather broad, flat, and asymmetric, we feel that an accurate experimental determination of the position of a T_1 minimum would be very difficult.

We wish to note that there is a quirk in the results for $\omega\tau_c \gg 1$ in the monovacancy $(c \to 1)$ limit. This quirk arises because there are two different frequency (or time) scales in the problem. One characteristic frequency is $\Gamma_c = 6\bar{c}\,\Gamma_0$, the mean-field rate for a specific particle to hop to any nearest neighbor. The other characteristic frequency is a vacancy frequency $\Gamma_v = 6\Gamma_0$, the rate for a vacancy to move to any nearest neighbor. Now $\bar{K}(\vec{q}, \omega)$ [see Eq. (26a)] scales as Γ_c but the frequency dependence of $\bar{K}(\vec{q}, \omega)$ is largely controlled by the dimensionless parameter ω/Γ_v. Although this distinction between frequency scales is largely irrelevant for most values of $\bar{c}$, it becomes vital as $\bar{c} \to 0$. For example, the mean-field approximation becomes exact for high enough frequencies which means $\omega \gg \Gamma_v$, not $\omega \gg \Gamma_c$. Thus for any fixed value of $\omega\tau_c = \omega/\Gamma_c$, the value of ω/Γ_v will always approach zero as $\bar{c} \to 0$ and one can never pass to the regime where $\omega \gg \Gamma_v$. This is the reason why $b_0(\infty)$ and $b_1(\infty)$ in the $c \to 1$ limit are not given by the mean-field approximation. For fixed but very small values of $\bar{c}$ the manifestation of these two frequency scales is the existence of three distinct frequency regimes: (i) low frequencies or $\omega \ll \Gamma_c$, (ii) intermediate frequencies or $\Gamma_c \ll \omega \ll \Gamma_v$, and (iii) high frequencies or $\Gamma_v \ll \omega$. In this situation T_{1m} occurs between regimes (i) and (ii) but T_1 will have a different asymptotic value in regime (iii) than it does in regime (ii).

In Fig. 1 we have plotted $1/g_0(\omega\tau_c)$, which is proportional to the angular averaged T_1, as a function of $\omega\tau_c$ for $c=0.85$ or $\bar{c}=0.15$. One feature of Fig. 1 that should be noted is that the asymptotic limits at high and low values of $\omega\tau_c$ indicated by the dashed straight lines in the figure, are not approached very quickly. For example, the value of T_1 is about 25% above the asymptotic limits when $T_1=3T_{1m}$. This type of behavior is not new to our theory and can be noted in other calculations.[2,8] The reason for it is that there is a distribution of relaxation rates in a BPP sense. This rather slow approach to the asymptotic limits is particularly insidious because over a limited range of $\omega\tau_c$, T_1 appears to approach incorrect asymptotic values. Further, the asymptotic value of T_1 at low frequencies is unusually sensitive to effects of a finite lattices with corrections proportional to $N^{-1/3}$, where N is the number of sites in the lattice. Thus computer simulations with a finite lattice could easily be in error by order $N^{-1/3}$ at low frequencies.

The other noteworthy feature in Fig. 1 is the very small glitch in the curve near $\omega\tau_c=0.14$. Since this glitch is barely larger than the inaccuracies in our numerical calculations, not very much weight should be attached to it. In fact, it is possible that it is an artifact of our numerical computations. On the other hand, similar glitches have been observed experimentally by Korn and Zamir.[13] Whether it is an artifact or not, the reason for the glitch is that the distribution of relaxation rates in a BPP sense is very dependent on both the magnitude and direction of $\vec{q}$, especially for values of $\vec{q}$ near the Brillouin-zone edge. The anisotropy as a function of the direction of $\vec{q}$ is considerably greater for the sc lattice than for other Bravais lattices and, for small concentrations of vacancies, is greater in the multiple-scattering approximation than in the mean-field approximation. These effects lead to a rather sharp change in the distribution of relaxation rates which, in turn, leads to a very weak glitch in T_1.

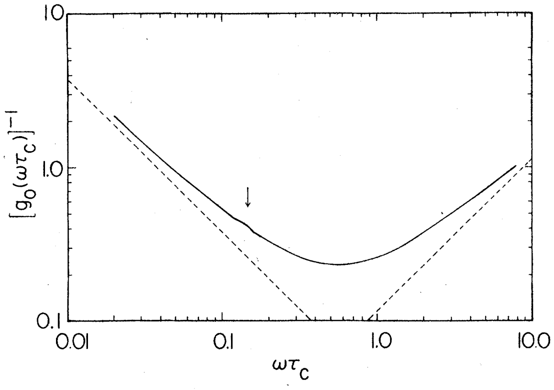

FIG. 1. Dimensionless function $[g_1(\omega\tau_c)]^{-1}$ vs $\omega\tau_c$ in the multiple-scattering approximation with $c=0.85$. This function is directly proportional [see Eq. (15)] to the angular averaged T_1. The arrow points to the small glitch in the curve which is discussed in the text. The dashed straight lines are the asymptotic limits for $\omega_c\tau$ sufficiently large and small.

There are a number of difficulties encountered when trying to fit a T_1 theory to experimental results. For instance, corrections due to conduction electrons can be significant or even dominant especially in the asymptotic regimes. Further, it is not obvious that Γ_0 must take the simple exponential form

$$\Gamma_0=\omega_0 e^{-E/kT}, \tag{29}$$

where ω_0 and E are independent of temperature, although it is widely believed to be valid if a single-diffusion mechanism causes the atomic motion in the entire temperature range considered. In our opinion, a temperature dependent ω_0 is certainly not impossible. It is also possible that measurements on both sides of the T_1 minimum are not experimentally accessible. If this occurs almost any theory can be made to fit the T_1 data alone even if T_1 is exponential in temperature. However, we wish to note that D/T_1 is independent of Γ_0 at high temperatures or low frequencies and that DT_1 is independent of Γ_0 at low temperatures on high frequencies. Since the diffusion coefficient D can be measured independently of T_1 by various magnetic field gradient techniques, a meaningful comparison between theory and experiment can be made even if both sides of the T_1 minimum are not experimentally accessible. The appropriate value of D can be obtained from Eqs. (24) and (25) while the asymptotic values of T_1 can be obtained from Eqs. (15), (17), and Table I.

One physical system that we know of where varying concentrations of particles are believed to hop around in a sc lattice is the system of protons in the γ phase of TiH_x. However, there is some dispute about whether the proton hopping is via nearest neighbor or not. Extensive T_1 measurements have been made on TiH_x by Korn and Zamir[13] at a variety of concentrations. We have tried to fit their data to our theory for $\text{TiH}_{1.7}$ ($c = 0.85$) with $a = 2.22$ Å since this is the case where they publish T_1 data with the conduction-electron contribution subtracted off. If we assume that Γ_0 is strictly exponential as in Eq. (29) and interpret the straight lines in their Fig. 3 as the asymptotic values of T_1 for $\omega\tau_c \gg 1$ and $\omega\tau_c \ll 1$, the values of ω_0 obtained from the two regimes differ by about a factor of 2. This discrepancy could be due to a number of things including the failure of the simple-hopping model or the possibility that the jumps are not to nearest neighbors. However, we also note that their $\ln(T_1)_d$ plot fits a straight line extremely well when $T_1 \geq 2T_{1m}$. Since our results predict T_1 should differ from its asymptotic values by about 40% when $T_1 = 2T_{1m}$, this could account for the discrepancy.

IV. CALCULATION OF $D_i(\vec{q},\omega)$

In this section we present the derivation and solution of the equations for $D_i(\vec{q}, \omega)$ in an approximation that we call the multiple-scattering approximation. Many of the equations used in this section can be taken directly from Ref. 14. [Reference 14 will hereafter be referred to as I and Eq. (n) of that paper will be referred to as Eq. (I-n).] In particular, we shall assume that the reader is acquainted with Secs. I and II of that paper. Although I describes a calculation pertaining to a one-dimensional system, many of the equations apply to any three-dimensional Bravais system with virtually no alterations except that the function which we call D_i here is denoted by $\bar{D}$ there.

The basis for our formalism is that all moments of any correlation function can be described by diagrammatic rules described elsewhere.[4] However, since one can neither evaluate or sum all of the moments exactly, one must devise a procedure to recognize, evaluate, and sum the most important contributions. In practice we have found it much easier to work with the self-energy or memory function $\bar{K}(\vec{q}, \omega)$ defined by the equation

$$[-i\omega + \bar{K}(\vec{q}, \omega)]\, D_i(\vec{q}, \omega) = 1\,, \tag{30}$$

than to work with $D_i(\vec{q}, \omega)$ directly. $\bar{K}(\vec{q}, \omega)$ can be interpreted as a wave-vector-dependent hopping frequency and [see Eq. (19a)] is equal to $\omega_c(\vec{q})$ in the mean-field approximation.

The approximation that we use is discussed in detail in I. Here we shall briefly describe it in a number of different ways. First, the approximation includes all moment diagrams for $\bar{K}$ that have one or fewer occupancy (solid) lines and one particle (dashed) lines. This diagrammatic method is described in I but, although it is an exact description, it is not very physical. In a scattering sense the approximation can be described as including the multiple scattering of the specific particle with a single vacancy (or other particle) exactly while the rest of the vacancies or particles are taken into account in a mean-field approximation.

The approximation is exact when $c \to 1$ because the specific particle can encounter only one vacancy at a time. The approximation is also exact when $c \to 0$. At intermediate concentrations we have checked the approximation by computing the first five moments of $\bar{K}$ exactly. For the sc lattice our approximation reproduces these moments to within 1%. Further, as discussed in Sec. II, our approximation yields a tracer correlation factor that is within 1% of the values obtained from computer simulations at all concentrations. Thus we believe that the approximation is good to within 1% at all values of $\vec{q}$ and ω.

Equations (I-5), (I-10), (I-20), (I-21), and (I-23)–(I-25) can be taken over from I directly. The only change is that $\Gamma_{\alpha\beta}$ is given by Eq. (9) instead of Eq. (I-16). Further, the Fourier transforms of functions of three independent-space variables can be defined in a manner analogous to Eq. (I-12). Thus, the Fourier transforms of Eqs. (I-10), (I-20), and (I-21) as applied to our problem are

$$\bar{K}(\vec{q}, \omega) = 4\bar{c}\Gamma_0 \sum_i \sin^2 \frac{1}{2}\, q_i a - 16\, c\, \bar{c}\, \Gamma_0^2 \times \sum_{i,j} G(s_i, s_j) \sin\tfrac{1}{2} q_i a \sin\tfrac{1}{2} q_j a\,, \tag{31}$$

$$G(s_i, s_j) = P(s_i, s_j) - 4c\Gamma_0 \sum_k P(s_i, s_k) G(s_k, s_j)\,, \tag{32}$$

and $P(\vec{q}',\vec{q}'')$ is the solution to the equation

$$P(\vec{q}', \vec{q}'') = N\delta(\vec{q}' - \vec{q}'') - 1 - N^{-1} \sum_{\vec{q}_1} H(\vec{q}', \vec{q}_1) P(\vec{q}_1, \vec{q}'')\,, \tag{33}$$

$$H(\vec{q}', \vec{q}'') = \Gamma_0 \{N\delta(\vec{q}' - \vec{q}'')\,[6(2-c) - f(\vec{q}_+') - \bar{c}f(\vec{q}_-')] - 6(2-c) - (2-c) f(\vec{q}' - \vec{q}'') + f(\vec{q}_+') + f(\vec{q}_+'') + \bar{c}f(\vec{q}_-') + \bar{c}f(\vec{q}_-'')\}\,. \tag{34}$$

In writing these equations we have used a certain amount of shorthand notation. We have suppressed the $\vec{q}$ and ω dependence of G, P, and H so that

$$G(\vec{q}', \vec{q}'') \equiv G(\vec{q}', \vec{q}'', \vec{q}; \omega)\,, \tag{35}$$

and similarly with P and H. We have also introduced the notation

$$G(t,r)=N^{-2}\sum_{\vec q',\vec q''} G(\vec q',\vec q'')t(\vec q')r(\vec q''), \tag{36}$$

where t and r are trigonometric functions of q' or q'' and s_i denotes $\sin q_i' a$, while c_i will be used to denote $\cos q_i' a$. $P(t,r)$ is defined similarly and finally $\vec q_\pm' = \vec q' \pm \frac{1}{2}\vec q$.

Although Eq. (33) appears to be very formidable, it is actually an integral equation whose kernel is a sum of separate terms. Further, a simple transformation simplifies the equation considerably. First we define

$$\tan p_i a = (1-\bar c)(\tan\tfrac{1}{2}q_i a)/(1+\bar c),$$

$$a_i = [(1+\bar c)\cos^2\tfrac{1}{2}q_i a + (1-\bar c)\sin^2\tfrac{1}{2}q_i a]^{1/2}, \tag{37}$$

consider $\{p_i\}$ and $\{a_i\}$ to be vectors, and define

$$\bar P(\vec q',\vec q'') = P(\vec q' - \vec p, \vec q'' - \vec p). \tag{38}$$

It is now straightforward (but tedious) to obtain the following equations:

$$P(s_i,s_j) = \delta_{ij}\cos^2 p_j a\,\bar P(s_i,s_j) + \sin p_i a \sin p_j a\,\bar P(c_i,c_j), \tag{39}$$

$$\bar P(s_i,s_i) = F(s_i^2)/[1-2(1+c)\Gamma_0 F(s_i^2)], \tag{40}$$

$$\bar P(c_i,c_j) = F(c_ic_j) + \Gamma_0\left([6(1+\bar c)F(c_i) - 2\sum_k a_k F(c_ic_k)2\bar P(1,c_j)] + \sum_k [2(1+\bar c)F(c_ic_k) - 2a_kF(c_i)]\bar P(c_k,c_j)\right), \tag{41}$$

$$\bar P(1,c_j) = F(c_j) + \Gamma_0\left(\sum_k [2(1+\bar c)F(1) - 2a_kF(c_k)]\bar P(1,c_j) + \sum_k [2(1+\bar c)F(c_k) - 2a_kF(1)]\bar P(c_k,c_j)\right). \tag{42}$$

Here we have introduced the notation

$$F(t) = N^{-1}\sum_{\vec q'} \frac{t(\vec q')}{-i\omega + \Omega_c(\vec q')}, \tag{43}$$

$$\Omega_c(\vec q') = 2\Gamma_0\left(3(2-c) - \sum_i a_i \cos q_i' a\right),$$

where, as in Eq. (36), t is a trigonometric function such as 1, $s_i^2 = \sin^2 q_i' a$, $c_i = \cos q_i' a$, or $c_ic_j = \cos q_i' a \cos q_j' a$. We note that F depends on $\vec q$ and ω as do $\bar P(t,r)$, $P(t,r)$, and $G(t,r)$ while $\vec a, \vec p$, and Ω_c depend on $\vec q$ but not on ω. The equations above now describe an algebraic solution to the problem. Once the appropriate summations for the F's are done $\bar P(s_i,s_j)$ is trivially evaluated and the solution to Eqs. (41) and (42) for $\bar P(c_i,c_j)$ is a 4×4 matrix inversion. Then one can proceed via Eqs. (38), (32), and (31) to the solution. The procedure is somewhat involved but not a very big job for modern computers.

Since the above equations must be solved for each value of $(\vec q,\omega)$, we have also investigated a number of purely numerical approximations. One such approximation, motivated by Padé approximations investigated earlier,[4] is given by Eq. (26b) where

$$p_1 = 2c\Gamma_0,$$

$$p_2(\vec q) = 2c\Gamma_0\,\omega_c(\vec q)/[\omega_c(\vec q) - \bar K(\vec q,0)], \tag{44}$$

and $\bar K(\vec q,0)$ is the memory function obtained from Eq. (31) with $\omega = 0$. By construction, this numerical approximation reproduces the solution to Eq. (31) exactly when $\omega \ll \Gamma_c$ or $\omega \gg \Gamma_0$. Also, by construction, the approximation is exact when $c\to 0$ or $c\to 1$. We have tested the approximation numerically for a number of values of $(\vec q,\omega)$ at various concentrations and found that it reproduces $D_i(\vec q,\omega)$ to within 3% for any $(\vec q,\omega)$ and all c and to within 2% if $c<0.7$. Over most of the $(\vec q,\omega)$ range the approximation is much better than this. Further, the approximation preserves the sum rule

$$\int_{-\infty}^{\infty}\frac{d\omega}{2\pi}D_i(\vec q,\omega) = 1. \tag{45}$$

We have also tested the numerical approximation

$$\bar K(\vec q,0) = 4\bar c\Gamma_0 f_t \sum_i \sin^2\frac{1}{2}q_i a, \tag{46}$$

where f_t is the exact tracer correlation factor. As can be easily seen, Eq. (46) is constructed to give the correct diffusion coefficient and to make $\bar K(\vec q,0)$ proportional to $\omega_c(\vec q)$. For $c\to 1$ this is a terrible approximation in that it introduces errors of up to 50% when $\vec q$ is near $(\pi,\pi,\pi)/a$. However, when $c<0.9$ it introduces errors of no more than 4%. Further Eq. (46) yield a $\bar K$ that is almost always too small. However, the numerical approximations given by Eq. (26b) with Eqs. (44) and (46) yield errors of no more than 4% if $c<0.9$ and about 2% of $c<0.7$. This obtains because the errors introduced by the two numerical approximations tend to cancel each other.

V. CALCULATION OF $D_{ij}(\vec{q},\vec{q}\,',\omega)$

In this section we shall investigate some approximations for $\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)$. As with D_i, it is also sometimes convenient to express D_{ij} in terms of a memory function or self-energy. In this case the appropriate form for the equation in configuration space is[15]

$$\begin{aligned}\frac{\partial}{\partial t}D_{ij}(\vec{R}_\alpha,\vec{R}_{\bar\alpha};\vec{R}_\beta,\vec{R}_{\bar\beta};t)&\\ +\sum_{\gamma\bar\gamma}\int d\bar{t}\,K(\vec{R}_\alpha,\vec{R}_{\bar\alpha};\vec{R}_\gamma,\vec{R}_{\bar\gamma};t-\bar{t})&\\ \times D_{ij}(R_\gamma,R_{\bar\gamma};R_\beta,R_{\bar\beta};\bar{t})&\\ =\delta_{\alpha\beta}\,\delta_{\bar\alpha\bar\beta}(1-\delta_{\alpha\bar\alpha})\delta(t)\,.&\qquad(47)\end{aligned}$$

If we Fourier transform this equation according to Eq. (8) we obtain the equation

$$\begin{aligned}-i\omega\tilde{D}_{ij}(\vec{q}\,',\vec{q}\,'',\omega)+N^{-1}\sum_{\vec{q}_1}\tilde{K}(\vec{q}\,',\vec{q}_1,\omega)\tilde{D}_{ij}(\vec{q}_1,\vec{q}\,'',\omega)&\\ =N[\delta(\vec{q}\,'-\vec{q}\,'')-1]\,,&\qquad(48\text{a})\end{aligned}$$

where $\tilde{K}$ is defined in terms of K in the same way that $\tilde{D}_{ij}$ is defined in terms of D_{ij} by Eq. (4).

The mean-field approximation for K in terms of $\Gamma_{\alpha\beta}$ has been derived elsewhere[15] and, after Fourier transforming, one obtains

$$\begin{aligned}\tilde{K}(\vec{q}\,',\vec{q}\,'',\omega)=2\bar{c}\,\Gamma_0\{N\delta(\vec{q}\,'-\vec{q}\,'')[6-f(\vec{q}\,')]-6&\\ -f(\vec{q}\,'-\vec{q}\,'')+f(\vec{q}\,')+f(\vec{q}\,'')\}\,.&\\ &\qquad(48\text{b})\end{aligned}$$

The most striking feature of Eqs. (48) is that in the mean-field approximation the equations for $\tilde{D}_{ij}$ are much more complex than are the equations for D_i. This is not entirely unexpected because D_i keeps track of only one specific particle while $\tilde{D}_{ij}$ must keep track of a pair of specific particles. In any case, Eqs. (48) describe an integral equation whose kernel is a sum of separable terms and thus obtaining a solution is straightforward. After a small amount of algebra one obtains

$$\begin{aligned}\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)=d_0(\vec{q},\omega)[N\delta(\vec{q}-\vec{q}\,')-1]+4\bar{c}\,\Gamma_0 d_0(\vec{q},\omega)\Bigg(\bigg(\sum_i d_0(\vec{q}\,',\omega)\sin q_i a\sin q_i' a\Big/[1-4\bar{c}\,\Gamma_0\bar{F}(s_i^2,\omega)]\bigg)&\\ +\Big(3-\sum_i\cos q_i a\Big)\bigg\{\Big[d_0(\vec{q}\,',\omega)\Big(1-\tfrac{1}{3}\sum_j\cos q_j' a\Big)-\bar{F}(1-c_x,\omega)\Big]\Big/[1-4\bar{c}\,\Gamma_0\bar{F}(3-6c_x+c_x^2+2c_xc_y,\omega)]\bigg\}&\\ +\Big[\sum_i(\cos q_i a-1)d_0(\vec{q}\,',\omega)\Big(\cos q_i' a-\tfrac{1}{3}\sum_j\cos q_j' a\Big)\Big]\Big/[1-4\bar{c}\,\Gamma_0\bar{F}(c^2x-c_xc_y,\omega)]\Bigg)\,.&\qquad(49)\end{aligned}$$

In this equation,

$$\bar{F}(t,\omega)=N^{-1}\sum_q t(\vec{q})\,d_0(\vec{q},\omega)\,,\qquad(50)$$

where t is a trigonometric function as in Sec. III and $d_0(\vec{q},\omega)$ is given by Eq. (23). The only part of $\tilde{D}_{ij}$ that contributes to T_1 (or T_2 or $T_{1\rho}$) is given by Eq. (22).

In most many-body problems the leading approximation ($\tilde{D}_{ij}^{(0)}$) to an exact two-particle correlation function ($\tilde{D}_{ij}$) would be the convolution of exact one-particle correlation functions. Because the center-of-mass coordinate has been integrated out in our case, this approximation would take the form

$$\tilde{D}_{ij}^{(0)}(\vec{q},\vec{q}\,',\omega)=N\delta(\vec{q}-\vec{q}\,')\int_{-\infty}^{\infty}\frac{d\bar\omega}{2\pi}\,D_i(\vec{q},\bar\omega)D_j(\vec{q},\omega-\bar\omega)\,.\qquad(51)$$

Other terms in $\tilde{D}_{ij}$ would arise because of the interactions between particles i and j. In fact, Eq. (49) describes just such a situation since $d_0(\vec{q},\omega)$ is the convolution described by Eq. (51), where D_i is given by the mean-field approximation. Thus, at least in this approximation, the first term in Eq. (49) describes each particle moving in its own mean field and the second term describes interactions or collisions between the particles.

Now the mean-field approximation for $D_i(\vec{q},\omega)$ can be in error by as much as 100% for concentrations near one so that Eq. (49) cannot be a very good approximation. However, motivated by the discussion in the previous paragraph we shall try to obtain better approximation for $\tilde{D}_{ij}$ by splitting the problem up. That is, we let

$$\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)=\tilde{D}_{ij}^{(0)}(\vec{q},\vec{q}\,',\omega)+\Delta\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)\,,\qquad(52)$$

where $\tilde{D}_{ij}^{(0)}(\vec{q},\vec{q}\,',\omega)$ is given by Eq. (51) but with $D_i(\vec{q},\omega)$ given by the exact (or the best we can obtain) single-particle correlation function. The corrections due to interactions between the two particles will then be included in $\Delta\tilde{D}_{ij}$. In fact this procedure is much more rigorous than just an analog to the mean-field approximation or an analog to other many-body theories. A rigorous expansion of $\tilde{K}(\vec{q},\vec{q}\,',\omega)$ in terms of its moments will yield some terms proportional to $N\delta(\vec{q}-\vec{q}\,')$. These terms will then produce exactly the term given by Eq. (51) for $\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)$.

The problem thus is reduced to finding a reasonable approximation for $\Delta\tilde{D}_{ij}$. As mentioned in Sec. II, the mean-field approximation $\Delta\tilde{D}_{ij}$ contributes about 11% of T_1 at low frequencies, about 18% at high frequencies, and less in between. We expect the situation to be similar with a better theory and thus $\Delta\tilde{D}_{ij}$ need not be calculated as precisely as $\tilde{D}_{ij}^{(0)}$. The approximation that we use for $\Delta\tilde{D}_{ij}$ is

$$\Delta\tilde{D}_{ij}(\vec{q},\vec{q}\,',\omega)=2\bar{c}\,\Gamma_0 d_0(\vec{q},\omega)f(\vec{q}-\vec{q}\,')\,d_0(\vec{q}\,',\omega)\,, \tag{53}$$

and the only part of this that contributes to T_1 is given in Eq. (27). The reasons for this choice are as follows. The lowest-order moment diagram that includes interactions between the two particles is given in Fig. (2g) or Fig. (3c) of Ref. 15. In Ref. 4, a procedure was described for turning moment diagrams into frequency and wave-vector-dependent contributions to correlation functions. The approximation described by Eq. (53) is an application of this procedure with the external lines replaced by mean-field single-particle correlation functions.

The relative accuracy of this approximation has been estimated in the following way. At all concentrations we have calculated the effects of a number of other converted moment diagrams. At low concentrations we find contributions from these other diagrams are of order 12% of the one which we have included. However, since $\Delta\tilde{D}_{ij}$ contributes less than 18% of T_1, this could be expected to introduce errors of about 2%. In fact, a comparison with the exact mean-field approximation shows this 2% to be correct.

As $c\to 1$, the contributions from these other diagrams are comparable to the contribution from the one diagram which we included. In this case, we appeal to a comparison with Wolf's results and find at most an 8% error in T_1 or $\tilde{D}_{ij}$. However, these diagrams that are important as $c\to 1$ decrease in magnitude drastically as c is lowered. In fact, they are typically reduced by a factor of two if $c<0.9$. Thus we estimate an error of about 4% if $c>0.9$. On the other hand, if Wolf's results are in error by 4% at low frequencies because of the effects of a finite lattice as discussed in Sec. III, our results are at most in error by 4% when $c\to 1$.

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[1] N. Bloembergen, E. M. Purcell, and R. V. Pound, Phys. Rev. 73, 679 (1948).

[2] H. C. Torrey, Phys. Rev. 92, 962 (1953); 96, 960 (1954).

[3] Dieter Wolf, Phys. Rev. B 10, 2710 (1974); D. Wolf, D. R. Figueroa, and J. H. Strange, *ibid.* 15, 2545 (1977).

[4] P. A. Fedders and O. F. Sankey, Phys. Rev. B 15, 3580 (1977); O. F. Sankey and P. A. Fedders, *ibid.* 15, 3586 (1977).

[5] See, for example, A. Abragam, *The Principles of Nuclear Magnetism* (Clarendon, Oxford, 1961).

[6] O. F. Sankey (unpublished).

[7] See, for example, J. M. Ziman, *Principles of the Theory of Solids*, 2nd ed. (Cambridge U.P., Cambridge, 1972), p. 37.

[8] C. A. Sholl, J. Phys. C 8, 1737 (1975).

[9] There are other terms in the expression for $\tilde{D}_{ij}$ that do not contribute to T_1. These terms that do not contribute prevent the particles from starting out or ending up at the same site. However, since the $T(\vec{R})$ are zero at $\vec{R}=0$, these terms are unnecessary. The full expression is given in Sec. IV.

[10] J. Bardeen and C. Herring, in *Imperfections in Nearly Perfect Crystals* (Wiley, New York, 1950).

[11] For a review and further references, see, C. P. Flynn, *Point Defects and Diffusion* (Clarendon, Oxford, 1972), Chap. 6.

[12] H. J. DeBruin and G. E. Murch, Philos. Mag. 27, 1475 (1973).

[13] Charles Korn and David Zamir, J. Phys. Chem. Solids 31, 489 (1970).

[14] P. A. Fedders, Phys. Rev. B 17, 40 (1978). This paper will hereafter be referred to as I and Eq. (n) of this paper will be referred to as Eq. (I-*n*).

[15] P. A. Fedders, Phys. Rev. B (to be published).