

# Moment-Method Calculation of Magnetization and Interspin-Energy<sub>in</sub> Diffusion

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The general moment-method calculation of diffusion is reviewed for the high-temperature long-wavelength limit. The temporal Fourier transform of the correlation function is assumed Lorentzian with a Gaussian cutoff. Exact expressions for the second and fourth moments are obtained as lattice sums over the spin-spin interactions. For a spin system with  $\mathcal{H} = \frac{1}{2} \sum_{i,j} A_{ij} \mathbf{I}_i \cdot \mathbf{I}_j$ , and  $A_{ij}$  nonzero only for  $i, j$  nearest neighbors, one has  $D = c A_{ij} b^2 / \hbar$ , where  $b$  is the nearest-neighbor distance and  $c = 0.328$  for the bcc lattice and 0.296 for the sc lattice; the latter agrees with a similar calculation by Mori and Kawasaki. For exchange-energy diffusion,  $c = 0.67$  for the bcc lattice. In a classical dipolar spin system, the exact moment method gives nearly the same result as the density matrix theory of Lowe and Gade. Reduction of diffusion by moderate quadrupolar interaction and diffusion energetics in an inhomogeneous field are discussed.

## I. INTRODUCTION

**S**PIN diffusion was first invoked by Bloembergen<sup>1</sup> to explain his measurements of  $T_1$  in impure ionic crystals. In crystals like these, ambiguous characterization of samples and theoretical complexity have combined to prohibit, until very recently, an experimental estimate of the diffusion coefficient. The first quantitative spin-diffusion measurement was apparently that of Reich,<sup>2</sup> in solid He<sup>3</sup>. His data were not very accurate, but agreed with the spin-diffusion coefficient which he guessed fairly accurately from the exchange interaction between spins, inferred from the exchange narrowing of the nuclear-resonance line. The present calculation was stimulated largely by the possible measurement of the diffusion coefficient in a type-II superconductor,<sup>3</sup> as suggested by Caroli and Matricon,<sup>4</sup> and by a careful series of measurements of the spin diffusion coefficient in He<sup>3</sup> by Thompson, Hunt, and Meyer<sup>5</sup> which established conclusively that spin flip-flop diffusion, rather than some other mechanism, was operative, and which allowed an accurate estimate of the diffusion coefficient.

In the above, magnetization is the entity which diffuses; in a large static magnetic field  $H_0$  energy and magnetization are proportional to each other and we call the diffusion coefficient  $D_Z$  ( $Z$  for Zeeman energy) in this case.

Ever since measurements of relaxation time  $T_1$  have been performed in zero field, it has been recognized<sup>6</sup> that mutual spin flips would also cause diffusion of interspin energy at a rate comparable to  $D_Z$  but different from it, different because both the thing diffusing

(spin-spin energy) and the diffusing interaction (untruncated spin-spin interaction) are different than in the case of the process described by Bloembergen. The same is true for spin diffusion in the case of strong rf field experiments analyzed in the rotating field.<sup>7</sup> We will not concern ourselves with these classical dipole cases because they are formidable to calculate, but rather with He<sup>3</sup>, where it is possible to observe nuclear resonance in an external field small compared to the interspin exchange interaction.<sup>2,8,9</sup> In that case, the small classical dipolar interaction between spins can couple Zeeman and exchange energies, and, if the external field is small, the easily observable Zeeman energy serves as a thermometer measuring the local spin-spin (exchange) temperature. The magnetization is then expected to appear to diffuse at a rate characteristic of exchange energy, and we call the diffusion coefficient  $D_E$  in this case. It has recently been measured in bcc He<sup>3</sup> by Thompson and Hunt.<sup>10</sup>

Many theoretical papers treat an imaginary Heisenberg paramagnet, having no dipolar interaction. In that case, at least in the high-temperature limit, the magnetization and the exchange energy diffuse completely independently of each other and of the applied uniform magnetic field (the latter because the field can always be transformed away using a rotating frame of reference without changing the Hamiltonian or density matrix).  $D_E$  is the thermal diffusivity in the zero-field limit. Apparently, it cannot be measured by neutron diffraction.

Theoretically, it is expected that

$$D_Z = c b^2 \omega_i, \quad (1)$$

where  $\omega_i$  is the root-mean-square spin-spin interaction between nearest spins (i.e., approximately  $T_2^{-1}$  in the

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<sup>1</sup> N. Bloembergen, *Physica* **15**, 386 (1949).

<sup>2</sup> H. A. Reich, *Phys. Rev.* **129**, 630 (1963).

<sup>3</sup> W. Fite and A. Redfield, *Phys. Rev.* **162**, 358 (1967).

<sup>4</sup> C. Caroli and J. Matricon, *Physik Kondensierten Materie* **3**, 380 (1965).

<sup>5</sup> J. R. Thompson, E. R. Hunt, and H. Meyer, *Phys. Letters* **25A**, 313 (1967).

<sup>6</sup> A. Redfield, *Phys. Rev.* **116**, 315 (1959). Errata: Insert  $(-1)^n$  before  $\bar{M}_{2n}$  on second line, p. 316; delete  $(-1)^n$  after Eq. (3).

<sup>7</sup> I. Solomon and J. Ezzraty, *Phys. Rev.* **127**, 78 (1962).

<sup>8</sup> R. L. Garwin and A. Landesman, *Phys. Rev.* **133**, A1503 (1964).

<sup>9</sup> A recent review was presented by H. Meyer *J. Appl. Phys.* **39**, 390 (1968).

<sup>10</sup> E. R. Hunt and J. R. Thompson, *Phys. Rev. Letters* **20**, 249 (1968).

classical dipolar case),  $b$  is the nearest-neighbor distance, and  $c$  is a number of order unity. A perturbation calculation of  $D_Z$  is not expected to be accurate because the spectral width of final states is of the same order of magnitude as the predicted flip-flop probability. Such a calculation has nevertheless been carried through by Lowe and Gade<sup>11</sup> for the classical dipolar case, on the reasonable grounds that there the flip-flop terms are half as large as the secular ( $S_{iz}S_{jz}$ ) terms of the spin-spin interaction, and that the perturbation limit might therefore not be too bad.

The moment method,<sup>6</sup> which we describe briefly below, was introduced by de Gennes<sup>12</sup> to obtain space-time correlations of fluctuations in magnetization in a paramagnet, measured experimentally by small-angle inelastic neutron diffraction, and related to spin diffusion by the fluctuation-dissipation theorem. Estimates of  $D_Z$  by the moment method<sup>12,13</sup> have been reviewed by Bennett and Martin<sup>14</sup> and by Résibois and DeLeener,<sup>15</sup> who have also estimated  $D_Z$  down to the critical point in a Heisenberg paramagnet (in which there is assumed zero dipolar interaction so that Zeeman and exchange energies are independent as long as  $M$  is small compared with the saturation magnetization). Except for these last two articles, all calculations assume the high-temperature limit, including ours. We calculate  $D_Z$  from an exact calculation of the first two nonzero moments; earlier papers are based on approximate fourth moments and treat only the exchange interaction in the sc lattice. Knowledge of the exact second and fourth moments does not yield an exact value for  $D_Z$ , since prediction of the latter depends on guessing a function  $g(\omega)$  whose second moment only is known from our calculation.

We also calculated  $D_E$  in the same way for bcc He<sup>3</sup>. The only previous calculation of  $D_E$  of which we are aware is that of Kawasaki.<sup>13</sup>

Spin diffusion should not be confused with spectral diffusion, which can occur when different spins are subjected to a local static field larger than the interspin interaction, the local static field being uncorrelated with position. There have been no simple satisfactory solutions to the spectral-diffusion problem, or, for that

matter, to the spin-diffusion problem in the presence of such inhomogeneous broadening.

## II. MOMENT METHOD

In a previous paper<sup>6</sup> the moment method was outlined based on a transient or time-domain argument; we here review it briefly in the frequency domain, using the same notation as much as possible. We first discuss diffusion of magnetization in high field to obtain  $D_Z$ ; we then describe how the argument is changed to calculate  $D_E$ .

In this method we assume without proof that the space-time variation of magnetization obeys a diffusion equation in the limit where the applied field is a uniform field plus an infinitesimal space-time varying field, its variations in space being smooth over a distance large compared to a lattice spacing, and, in time, slow compared to a spin-flip time. We then seek an expression for the linear response of the system which is consistent with this equation and is also in accord with the high-frequency response of the system (still for slow space variation) as constrained by expressions for frequency moments of energy absorption, obtained just as Broer<sup>16</sup> obtained the absorption moments in the paramagnetic absorption experiments of Gorter and co-workers. The low-frequency diffusion assumption and the high-frequency predictions are reconciled in the same way as exchange narrowing was treated by Van Vleck,<sup>17</sup> and by Anderson and Weiss.<sup>18</sup> The assumption of diffusion, and the final state implied thereby, should not be taken lightly because it has been conjectured that spin diffusion may be quenched in the case of large inhomogeneous broadening.<sup>19</sup>

We suppose that a large field  $H_0\hat{z}$  has induced a magnetization  $M_0$  as a result of spin-lattice relaxation which will thereafter be neglected as infinitely slow. At some time an infinitesimal space-time varying field is applied, one of whose Fourier components can be written

$$h(x, t) = H_1 \cos \omega t \sin kx. \quad (2)$$

This field is assumed to be in the  $z$  direction, in violation of Maxwell's equations, which is probably not significant since transverse components omitted in (2) only tilt the field slightly if  $H_0$  is large.

In the linear limit, this Fourier component can be treated by itself. If  $\omega=0$ , the dc response of the system a long time after (2) is applied, and after spin diffusion has equalized the Zeeman temperature, will be  $M = M_0 + m(x)$ , where  $m(x) = \chi_0 h(x)$ . Here  $\chi_0 = M_0/H_0$ , or, more generally,  $\chi_0$  is the ratio of  $\langle M \rangle$  to  $H_0$ , where  $\langle \rangle$  denotes space average. The magnetization is expected to obey a diffusion equation consistent with this long-

<sup>11</sup> I. J. Lowe and S. Gade, Phys. Rev. **156**, 817 (1967). A related experiment is described by D. Tse and I. J. Lowe, Phys. Rev. (to be published).

<sup>12</sup> P. G. de Gennes, J. Phys. Chem. Solids **4**, 223 (1958). For more recent work and references on neutron diffraction, see M. F. Collins and W. Marshall, Proc. Phys. Soc. (London) **92**, 390 (1967); also, M. F. Collins, J. Appl. Phys. **39**, 533 (1968). Collins and Marshall point out an arithmetical error in de Gennes's simple cubic value for  $M_4$ ; their expression for  $M_4$  for arbitrary  $k$  agrees with our Eqs. (14) and (23) in the small- $k$  limit.

<sup>13</sup> H. Mori and K. Kawasaki, Progr. Theoret. Phys. (Kyoto) **27**, 529 (1962); K. Kawasaki, *ibid.* **29**, 801 (1963).

<sup>14</sup> H. S. Bennett and P. C. Martin, Phys. Rev. **138**, A608 (1965).

<sup>15</sup> P. Résibois and M. DeLeener, Phys. Letters **25A**, 65 (1967); Phys. Rev. **152**, 305 (1966); **152**, 318 (1966); J. Kocinski, Phys. Letters **25A**, 92 (1967).

<sup>16</sup> L. J. F. Broer, Physica **10**, 801 (1945).

<sup>17</sup> J. H. Van Vleck, Phys. Rev. **74**, 1168 (1948).

<sup>18</sup> P. W. Anderson and P. R. Weiss, Rev. Mod. Phys. **25**, 269 (1953).

<sup>19</sup> P. W. Anderson, Phys. Rev. **109**, 1492 (1958).

time equilibrium:

$$\partial M_z / \partial t = D_Z \nabla^2 (M_z - \chi_0 H_z),$$

$$H_z = H_0 + h(x, t).$$

If the small field (2), with  $\omega=0$ , is turned off after equilibrium is reached, the magnetization will decay back to its uniform state exponentially with time constant  $\tau = 1/D_Z k^2$ . If, on the other hand, (2) is applied continuously with  $\omega \neq 0$ , the response will be Debye-like appropriate to the time constant  $\tau$ :

$$m(x, t) = \chi_0 H_1 \frac{\sin kx}{1 + \omega^2 \tau^2} (\cos \omega t + \omega \tau \sin \omega t). \quad (3)$$

To make contact with the moment method, we calculate the rate at which energy is absorbed by the spin system from the coils which produce the field (2); this is the space-time average of  $h \partial m / \partial t$ . The average power absorption per unit volume is

$$E_D(\omega, k) = \frac{1}{4} H_1^2 \chi_0 \omega^2 \tau / (1 + \omega^2 \tau^2). \quad (4)$$

For large  $\omega$ , the energy absorption is a constant function of  $\omega$ , according to this reasoning; in the limit  $k \rightarrow 0$ ,  $Ek^{-2}$  is a constant except for a region  $k^2 D_Z$  near zero frequency, in realistic cases a region encompassing at most a few cycles.

This cannot be true for large  $\omega$ , since there are no transitions possible for  $\omega \gg \gamma H_0$ . In fact, the absorption must drop to zero for frequencies near the spin-spin interaction frequency, just as it does in the case of zero-field paramagnetic absorption as discovered by Gorter and co-workers. Thus the true absorption is expected to be given by

$$E(\omega, k) = E_D(\omega, k) g(\omega), \quad (5)$$

where  $g(0)=1$  and  $g(\omega)$  is positive and decreases to zero as  $\omega \rightarrow \infty$ .

We use  $\alpha, \beta$  to label eigenstates of the system in the uniform field  $H_0$ , and define  $P_{\alpha\beta}$  as the matrix element of the time-dependent perturbation

$$P = \sum_i h(x_i, t) S_{iz}, \quad (6)$$

where  $i$  labels different spins.  $|P_{\alpha\beta}|^2$  is thus proportional to the transition rate between states  $\alpha$  and  $\beta$ , induced by  $P$ .

The ratio of two moments of the absorption is

$$\frac{\int_0^\infty \omega^{2n} E(k, \omega) d\omega}{\int_0^\infty \omega^{2m} E(k, \omega) d\omega} = \frac{\sum_{\alpha\beta} (\omega_\alpha - \omega_\beta)^{2n+2} |P_{\alpha\beta}|^2}{\sum_{\alpha\beta} (\omega_\alpha - \omega_\beta)^{2m+2} |P_{\alpha\beta}|^2}, \quad (7)$$

where  $\omega_\alpha$  is the energy of state  $\alpha$ , divided by  $\hbar$ . The expression differs from the familiar Van Vleck<sup>17</sup> moment expressions by the extra factors of  $(\omega_\alpha - \omega_\beta)^2$  on the right. These<sup>18</sup> arise whenever absorption is not confined to a narrow line and come from the fact that the rate of energy absorption associated with two levels is proportional to the transition probability times the energy

absorbed per transition  $\hbar(\omega_\alpha - \omega_\beta)$  and also times the thermal occupation probability difference  $\hbar(\omega_\alpha - \omega_\beta)/kT$  (in the high-temperature limit). We define

$$M_{2n} = \frac{\sum_{\alpha\beta} (\omega_\alpha - \omega_\beta)^{2n} |P_{\alpha\beta}|^2}{\sum_{\alpha\beta} |P_{\alpha\beta}|^2}. \quad (8)$$

These moments can be calculated, at least in principle. We also have

$$M_2 = \int \frac{\omega^2 \tau^2}{1 + \omega^2 \tau^2} g(\omega) d\omega \bigg/ \int \frac{\tau^2}{1 + \omega^2 \tau^2} g(\omega) d\omega. \quad (9)$$

In the numerator the integrand can be replaced by  $g(\omega)$  because, as mentioned above, the other term is different from unity only for very low frequency; and likewise in the denominator  $g(\omega) \cong 1$  in the range where the other, Lorentzian, term is appreciable. Thus

$$M_2 \cong \frac{\int g(\omega) d\omega}{\int [\tau^2 / (1 + \omega^2 \tau^2)] d\omega} = (2/\pi\tau) \int_0^\infty g(\omega) d\omega; \quad (10)$$

likewise

$$\frac{M_4}{M_2} \cong \frac{\int_0^\infty \omega^2 g(\omega) d\omega}{\int_0^\infty g(\omega) d\omega}. \quad (11)$$

All the higher moments of  $g(\omega)$  can likewise be calculated, in principle. In practice one calculates only  $M_2$  and  $M_4$  and guesses a form for  $g(\omega)$  consistent with these two moments. We assume<sup>12,17</sup> that  $g(\omega)$  is Gaussian because a Gaussian has finite moments, is mathematically tractable, and has been successful in other similar cases.

Of course, the form of  $g(\omega)$  depends on the Hamiltonian, and may well be radically different from a Gaussian. We have mentioned that diffusion may not occur, or may be strongly inhibited, in the case of inhomogeneous broadening.<sup>19</sup> In that case  $g(\omega)$  might have a delta function at  $\omega=0$ , or a strong peak near  $\omega=0$ , and such a peak would not be easy to predict from the moments of  $g(\omega)$ . For the cases treated in this paper we believe that diffusion does occur, and therefore that  $g(\omega)$  is well behaved near  $\omega=0$ . Inspection of the expressions<sup>6</sup> for the high moments suggests that for these cases the ratio  $M_{2n+2}/M_{2n}$  is not strongly dependent on  $n$ , consistent with a finite-range function like a Gaussian. If  $g(\omega)$  is assumed to be a step function, the predicted  $D_Z$  is decreased by a factor of only 0.72 compared with the prediction (12) below.

Assuming  $g(\omega)$  is a Gaussian,  $D_Z$  is then determined by (10), (11), and the equation  $\tau^{-1} = Dk^2$  as

$$D_Z = (M_2/k^2) (\pi M_2/2M_4)^{1/2}. \quad (12)$$

Equation (8) becomes,<sup>6</sup> after converting the sums to traces of commutators, and assuming a uniform spatial distribution of one species of spin (100% abundant),

$$M_2 = \frac{\frac{1}{2} k^2 \sum_{ij} x_{ij}^2 \text{Tr}[\mathcal{H}, S_{iz}][\mathcal{H}, S_{jz}]}{\hbar^2 \text{Tr} S_{iz}^2}, \quad (13)$$

where  $x_{ij}^2 = x_i - x_j$ , and  $\mathcal{H}$  is the Hamiltonian of the system in a uniform field.

Likewise,

$$-\frac{M_2}{M_4} = \frac{\hbar^2 \sum_{ij} x_{ij}^2 \text{Tr}[\mathcal{H}, S_{iz}][\mathcal{H}, S_{jz}]}{2 \sum_{ij} x_{ij}^2 \text{Tr}[\mathcal{H}, [\mathcal{H}, S_{iz}]] [\mathcal{H}, [\mathcal{H}, S_{jz}]]}. \quad (14)$$

This completes the general theory. We will not attempt to justify or discuss it further.

Of course, in general,  $D_Z$  is a tensor for the dipolar interaction even in a cubic crystal, and for the exchange interaction in noncubic crystals. The  $x$ - $z$  component of the  $D_Z$  tensor, for example, relating diffusion in the  $x$  direction to the magnetization gradient in the  $z$  direction, would be obtained by replacing  $x_{ij}^2$  with  $x_{ij}z_{ij}$  in (13) and (14).

We now turn to the calculation of  $D_E$ , which is a simple generalization of the above. Although a more general discussion is easy, we specialize our treatment to  $\text{He}^3$  in zero applied field, where the dominant interaction is exchange between nearest-neighbor spins only; it is reasonable that next- and further-neighbor interactions are negligible. For the Bravais lattices we discuss, this exchange is the same between all spins. Now assume the crystal is subjected to some space-time varying deformation; this will produce a space-time modulation of the exchange interaction of the form

$$\tilde{P} = \epsilon_1 \sum_i E_i \cos \omega t \sin k x_i, \quad (15)$$

where  $E_i$  is an operator whose expectation value is the unperturbed exchange associated with spin  $i$ ;

$$E_i = \sum_k A_{ik} \mathbf{S}_i \cdot \mathbf{S}_k. \quad (16)$$

Here  $A_{ik}$  is the unperturbed exchange interaction between spins  $i$  and  $k$ , so that the exchange Hamiltonian in this case is  $\mathcal{H} = \frac{1}{2} \sum_i E_i$ . The constant  $\epsilon_1$  is proportional to the imposed ac strain variation. The exchange interaction  $A_{ik}$  is zero unless  $i$  and  $k$  are nearest neighbors; then it is some constant  $A$  for all nearest-neighbor pairs. The perturbation (15), like (6), is artificial since any real lattice deformation would involve shear as well as the pure compression implied in (15).

The response of the system as a result of diffusion is to make the expectation value of  $E_i$  vary as  $\sin k x_i$  spatially, and periodically with period  $\omega$ , temporally. In fact, all the reasoning leading to (12) follows with  $S_{iz}$  and  $S_{jz}$  replaced by  $E_i$  and  $E_j$  in the expressions for  $M_2$  and  $M_4$ , (13) and (14). This completes our general derivation of  $D_E$ .

Note that at extremely low temperatures the thermal conductivity of the spin system would produce attenuation of phonons, just as thermal conductivity of a gas does for ultrasonic waves. Conversely, phonons could relax the exchange system via the same mechanism—an effect which we have not seriously studied but believe to be negligible.

We next discuss the case of  $\text{He}^3$  in a field comparable to  $A/\hbar\gamma$ , the exchange-interaction field. In the high-temperature limit, the ratio of the expectation values of the exchange and Zeeman energies in a uniform field, at thermal equilibrium, is expressed in terms of a local field  $H_L$ ;

$$\frac{\langle \frac{1}{2} \sum E_i \rangle}{\langle \hbar\gamma H_0 \sum S_{iz} \rangle} = \frac{H_L^2}{H_0^2} = \frac{\text{Tr}(\frac{1}{2} \sum E_i)^2}{\text{Tr}(\hbar\gamma H_0 \sum S_{iz})^2}. \quad (17)$$

This ratio is maintained at this value by the weak classical dipolar interaction with a cross-relaxation time of less than 1 sec if  $H_L \approx H_0$  in  $\text{He}^3$ . If diffusion is measured over a time scale slow compared to this cross relaxation rate, this ratio would be maintained and the diffusion coefficient is expected to be the average of  $D_Z$  and  $D_E$  weighted against the relative contribution to the total energy (taking as zero energy a completely disordered spin system). We thus expect that

$$D = (D_Z H_0^2 + D_E H_L^2) / (H_0^2 + H_L^2). \quad (18)$$

The denominator of (18) is proportional to the heat capacity of the spin system, the numerator to its thermal conductivity. More generally, the behavior of the system might be described by two diffusion equations, for exchange energy and for Zeeman energy, connected by spatially local cross relaxation.

Finally, we should mention that spin-echo experiments in  $\text{He}^3$  usually measure the diffusion of transverse magnetization  $M_x$ ,  $M_y$  whereas we have defined  $D_Z$  above as the diffusion coefficient of  $M_z$ . From the rotation invariance of the exchange interaction it is easy to show (by transforming away the dc field with a rotating coordinate transformation) that space varying transverse magnetization will diffuse with the same coefficient as  $M_z$  in a uniform field. The measurements are performed in a nonuniform field, however, but it is reasonable, though not proven, that the usual spin-echo diffusion measurements yield the same diffusion coefficient as long as the field variation between neighboring spins is small compared with the exchange interaction, as it always will be. Diffusion of  $M_z$  could be measured by the stimulated-echo method.

For a classical dipolar solid, the diffusion coefficient of  $M_x$  and  $M_y$  in the presence of steady rf irradiation<sup>7</sup> is different from that of  $M_z$  (with no irradiation). It could be calculated by generalizations of the methods used to calculate  $D_Z$  and  $D_E$ .

### III. COMMUTATORS AND TRACES

#### A. Magnetization Diffusion

The most complicated part of the calculation of  $D_Z$  and  $D_E$  is the calculation of the traces appearing in  $M_2$  and  $M_4$ ; the lattice sums subsequently needed are relatively simple.

We write the truncated Hamiltonian as

$$\mathcal{H} = \frac{1}{2} \sum_{kl} (A_{kl} S_{k+} S_{l-} + B_{kl} S_{kz} S_{lz}) + \sum_k \hbar \gamma H_0 S_{kz}. \quad (19)$$

For the classical dipolar interaction,<sup>17</sup>  $B_{kl} = -2A_{kl}$ ; both fall off as the cube of the distance between  $k$  and  $l$ , with the well-known  $P_2(\cos\theta)$  angular dependence. For He<sup>3</sup>,  $B_{kl} = A_{kl}$ .

The commutators needed are

$$\begin{aligned} [\mathcal{H}, S_{iz}] &= -\frac{1}{2} \sum_k A_{ik} (S_{i+} S_{k-} - S_{i-} S_{k+}); \quad (20) \\ 2[\mathcal{H}, [\mathcal{H}, S_{iz}]] &= \sum_k A_{ik} \{ 2A_{ik} (S_{iz} S_{k+} S_{k-} - S_{kz} S_{i+} S_{i-}) \\ &\quad + B_{ik} S_{iz} (S_{i+} S_{k-} + S_{i-} S_{k+}) - B_{ik} (S_{i+} S_{k-} + S_{i-} S_{k+}) S_{kz} \\ &\quad + \sum_l [A_{il} S_{iz} (S_{k+} S_{l-} + S_{k-} S_{l+}) \\ &\quad - A_{kl} S_{kz} (S_{l+} S_{i-} + S_{l-} S_{i+}) \\ &\quad + (B_{lk} - B_{li}) S_{lz} (S_{i+} S_{k-} + S_{i-} S_{k+}) \} \}. \quad (21) \end{aligned}$$

Henceforth in this paper, all sums over indices are *restricted* in that no index of summation can equal any other index of summation or other index ( $i$  in the above) in the summand. Mathematically, in the sums in (21),  $i \neq k \neq l \neq i$ . Sums are not restricted in the sense that permutations of the same spins over different indices are all included; thus the factor of  $\frac{1}{2}$  in (19) is included since each pair of spins occurs twice in the sum.

The commutators above, and traces below, are much simpler for a spin- $\frac{1}{2}$  Heisenberg paramagnet. In that case, vector notation is useful and the resulting calculation can be used as a check.

The traces need are

$$\begin{aligned} \frac{\text{Tr}[\mathcal{H}, S_{iz}][\mathcal{H}, S_{jz}]}{\text{Tr} S_{iz}^2} &= \frac{2}{3} S(S+1) A_{ij}^2; \quad (22) \\ \frac{\text{Tr}[\mathcal{H}, [\mathcal{H}, S_{iz}]][\mathcal{H}, [\mathcal{H}, S_{jz}]]}{\text{Tr} S_{iz}^2} &= \frac{2}{9} S^2 (S+1)^2 \\ &\times \{ \sum_k 3A_{ik}^2 A_{jk}^2 - A_{ij}^2 [4A_{ik}^2 + 4A_{jk}^2 + (B_{ik} - B_{jk})^2] \\ &\quad + 2A_{ik} A_{jk} A_{ij} (B_{ik} + B_{jk} - 2B_{ij}) \} - [S(S+1)/15] \\ &\times [10A_{ij}^4 + (2S-1)(2S+3)A_{ij}^2 (B_{ij}^2 + 4A_{ij}^2)], \quad (23) \end{aligned}$$

where  $i \neq j$  and the sums over  $k$  are restricted as mentioned above. Collins and Marshall<sup>12</sup> have obtained essentially the same result.

The second trace simplifies greatly when applied to bcc He<sup>3</sup> since  $S = \frac{1}{2}$ ,  $B_{ik} = A_{ik}$ , all  $A_{ik}$  are equal and assumed nonzero only if  $i$  and  $k$  are near neighbors, and, least trivially, there are no three spins which are all mutually near neighbors in the bcc lattice. Thus terms involving  $A_{ij} A_{ik} A_{jk}$  are zero for this lattice (also for the sc lattice) while the last term is zero for  $S = \frac{1}{2}$ .

Then (23) becomes

$$\begin{aligned} \text{Tr}[\mathcal{H}, [\mathcal{H}, S_{iz}]][\mathcal{H}, [\mathcal{H}, S_{jz}]] \\ = \sum_k A^2 \{ -\frac{5}{3} A_{ij} (A_{jk} + A_{ik}) \\ + \frac{3}{2} A_{ik} A_{jk} \} - \frac{1}{2} A_{ij}^4. \quad (23') \end{aligned}$$

Here and later we write terms like  $A_{ij}^2 A_{kl}$  as  $AA_{ij} A_{kl}$ , where  $A$  is the value  $A_{ij}$  assumes when  $i$  and  $j$  are near neighbors.

## B. Interspin-Energy Diffusion

Here we specialize the calculation to bcc He<sup>3</sup>, using the exchange Hamiltonian [i.e.,  $B_{kl} = A_{kl}$  in (19)]. Vector notation shortens the calculation. For this Hamiltonian ( $\mathcal{H} = \frac{1}{2} \sum_i E_i$ ) the second-moment commutator and trace are, for  $S = \frac{1}{2}$ ,

$$[\mathcal{H}, E_i] = -i \sum_{kl} A_{ik} (A_{kl} - A_{il}) (\mathbf{S}_l \times \mathbf{S}_k \cdot \mathbf{S}_i), \quad (24)$$

$$\frac{\text{Tr}[\mathcal{H}, E_i][\mathcal{H}, E_j]}{\text{Tr} E_i^2} = \frac{\frac{1}{8} \sum_k A_{ik}^2 A_{jk}^2}{\frac{1}{4} \sum_k A_{ik}^2}. \quad (25)$$

The  $A_{il}$  term in (24) sums to zero because of the antisymmetry of the vector product under interchange of  $k$  and  $l$ .

The double commutator needed in the fourth-moment computation is lengthy but is simplified when the no-two-mutual-nearest-neighbor property of the lattice is used to eliminate terms. It is

$$\begin{aligned} [\mathcal{H}, [\mathcal{H}, E_i]] &= \frac{1}{2} A \sum_{kl} A_{ik} A_{kl} \mathbf{S}_k \cdot (\mathbf{S}_i - \mathbf{S}_l) \\ &\quad + \sum_{klm} [-A_{ik} A_{kl} A_{lm} (iklm) + A_{mi} A_{ik} A_{kl} (miki) \\ &\quad - A_{ik} A_{lk} A_{mk} (ilmk)]. \quad (26) \end{aligned}$$

Here  $(iklm)$  is shorthand for  $\mathbf{S}_i \times \mathbf{S}_k \cdot \mathbf{S}_l \times \mathbf{S}_m$ .

A long calculation, with much cancellation of terms but no tricks other than omission of three nearest-neighbor terms, yields

$$\begin{aligned} \text{Tr}[\mathcal{H}, [\mathcal{H}, E_i]][\mathcal{H}, [\mathcal{H}, E_j]] &= 2^N (3/64) A^2 \\ &\times \{ -2A^2 \sum_k A_{ik} A_{kj} + A \sum_{kl} [2A_{ik} A_{kl} A_{lj} + 2A_{ki} A_{ij} A_{jl} \\ &\quad - 2A_{ij} A_{jk} A_{kl} - 2A_{kl} A_{li} A_{ij} - \frac{5}{2} A_{ik} A_{jk} A_{lk} - A_{ik} A_{kj} A_{jl} \\ &\quad - A_{ki} A_{il} A_{lj}] + 2 \sum_{kl} A_{ik} A_{kj} A_{jl} A_{li} \}. \quad (27) \end{aligned}$$

## IV. EVALUATION AND COMPARISON WITH EXPERIMENTS

### A. Solid He<sup>3</sup>

The lattice sums in the case of He<sup>3</sup> are quite simple because there are a finite number of terms. It is perhaps worth mentioning some identities which apply to the bcc lattice and which may possibly be useful in other

cases. The first is

$$\sum_{jk} x_{ij}^2 A_{ik} A_{jk} = 2 \sum_{jk} x_{ij}^2 A_{ij} A_{jk} + 2 \sum_j x_{ij}^2 A_{ij}^2. \quad (28)$$

This is proven by rewriting  $x_{ij}^2$  on the left, as  $(x_{ik} + x_{kj})^2$ , and noticing that the cross term  $x_{ik}x_{kj}$  will sum to zero for any Bravais lattice if  $j$  and  $k$  are unrestricted. The right side is obtained by relabelling indices of summation and adding the last term so that the  $ijk$  sum on the right can be restricted again. Equation (28) further simplifies to

$$\sum_{jk} x_{ij}^2 A_{ik} A_{jk} = 16 \sum_j x_{ij}^2 A_{ij}^2, \quad (28')$$

since 16 is twice the bcc coordination number, and  $A_{ik}$  and  $A_{jk}$  equal  $A_{ij}$  or zero.

Another identity based on a more involved but similar proof is

$$\sum_{klj} x_{ij}^2 A_{ik} A_{kl} A_{lj} = (3C^2 - 2C + 1) A^2 \sum_j x_{ij}^2 A_{ij}, \quad (29)$$

where  $C$  is the coordination number of the lattice.

The result of the summation for the bcc lattice is

$$M_2 = (4b^2/6\hbar^2) b^2 A^2, \quad (30)$$

$$M_4/M_2 = 13A^2/2\hbar^2, \quad (31)$$

$$D_Z = 0.328(b^2 A/\hbar), \quad (32)$$

where  $b$  is the nearest-neighbor distance.

This agrees well with the experiment of Thompson *et al.*,<sup>5</sup> who find

$$D_Z = (0.35 \pm 0.03) b^2 A/\hbar. \quad (33)$$

The same calculation for a sc lattice yields  $D_Z = 0.296b^2 A/\hbar$ , which is about 3% greater than the highest previous estimate<sup>13</sup> and 31% higher than the lowest previous estimate.<sup>14</sup> These estimates are based on a Gaussian assumption for  $g(\omega)$  and differ only in approximations or errors in the evaluation of  $M_4$ .

Turning to exchange-energy diffusion, the quantity corresponding to  $M_2$  is exactly twice as large as in the case of Zeeman diffusion for the bcc lattice. For the sc lattice it is also twice as large, and this is a general property of any Bravais lattice.

The bcc sum corresponding to  $M_4/M_2$  is  $25A^2/4\hbar^2$ , that is, nearly the same as the Zeeman value. It is by no means obvious that these quantities should be nearly the same. Thus for the bcc lattice

$$D_E = 0.67 Ab^2/\hbar. \quad (34)$$

Thompson and Hunt<sup>10</sup> have measured  $D_E$  in solid He<sup>3</sup> and found it to be  $(0.75 \pm 0.15) Ab^2/\hbar$ , in good agreement with our result.

## B. Classical Dipolar Interaction

### Perturbation Limit of $D_Z$

The evaluation of  $M_4$  for pure dipolar interaction would involve a lengthy evaluation and summation of

(23) according to (14). While this is possible, it does not seem worthwhile in view of the lack of precise experiments and the remaining theoretical arbitrariness in the choice of the form of  $g(\omega)$ .

If we assume artificially that  $A_{kl}$  is much smaller than  $B_{kl}$  in the Hamiltonian (19), then our theory should give the perturbation limit result provided that  $g(\omega)$  can be taken as Gaussian in that case, as seems reasonable. If  $B \gg A$ , then only the  $B^2 A^2$  terms in  $M_4$  need be retained, while  $M_2$  is the same. The resulting prediction is

$$D_Z = \hbar^{-1} \left[ \frac{\pi (\sum_j x_{ij}^2 A_{ij}^2)^3 S(S+1)}{12 \sum_{jk} x_{ij}^2 A_{ij}^2 (B_{ik} - B_{jk})^2} \right]^{1/2}. \quad (35)$$

This is identical to the result of Lowe and Gade<sup>11</sup> in the same limit. This can be simplified while introducing little error by unrestricted the sum to permit  $k=i$  or  $j$ ; and assuming the cross sum involving  $-2B_{ik}B_{jk}$  is small. Then (35) becomes

$$D_Z \cong \frac{\pi^{1/2} S(S+1) \sum_j x_{ij}^2 A_{ij}^2}{4\hbar^2 \langle \Delta\omega^2 \rangle^{1/2}}, \quad (35')$$

where  $\langle \Delta\omega^2 \rangle^{1/2}$  is the Van Vleck second moment<sup>16</sup> of the high-field transverse resonance line.

The value of  $D_Z$  which would be calculated using the exact expression (23) is probably very close to this, because in (23) it is probably permissible to drop all terms involving the first power of  $A_{ij}$ ,  $B_{ik}$ , etc. These will tend to average to zero because of the angular variation of  $A_{ij}$ , after summation. The first term of (23), on summation, can be operated on with an identity similar to (28); and if  $B_{ij} = -2A_{ij}$ , then (23) can be written, for  $S = \frac{1}{2}$ ,

$$\begin{aligned} & -\text{Tr}[\mathcal{H}, [\mathcal{H}, S_{iz}]] [\mathcal{H}, [\mathcal{H}, S_{jz}]] / \text{Tr} S_{iz}^2 \\ & \cong \frac{1}{9} 4 S^2 (S+1) \sum_k A_{ij}^2 B_{jk}^2 \\ & + \frac{1}{9} [S^2 (S+1)^2] (5 A_{ij}^2 B_{ij}^2 - \sum_k A_{ik}^2 B_{jk}^2). \end{aligned} \quad (23')$$

This is not supposed to be correct for given  $i$  and  $j$ , but is expected to give the correct answer after summation over  $i$  and  $j$ . The last two terms largely cancel, and in any case are small compared to the first term, which leads to (35').

In many cases it is sufficient to estimate the average of  $D_Z$  with respect to the angle between the crystal axes and the magnetic field. It is simple, and not too inaccurate, to replace  $\langle \Delta\omega^2 \rangle$  by its angle average. It is easy to average the numerator in (35'), using the fact that the angle average of  $x_{ij}^2 (1 - 3 \cos^2 \theta_{ij})^2$  is  $4r_{ij}^2/21$ , from simple integration. Then the angle average of  $D_Z$  is

$$D_Z = \frac{\pi^{1/2}}{84} \frac{S(S+1) \gamma^4 \hbar^2 \sum_j r_{ij}^{-4}}{\langle \Delta\omega^2 \rangle^{1/2}}. \quad (35'')$$

In the above, we considered diffusion of  $M_z$  in a gradient transverse to  $H_0$ . Diffusion is faster along the

$z$  axis, and is calculated by replacing  $x_{ij}^2$  by  $z_{ij}^2$  in the above. This yields a diffusion coefficient 11/5 times larger than in the  $x$  or  $y$  directions.

The average of  $D_Z$  with respect to direction of diffusion relative to the dc field, that is,  $\frac{1}{3}$  the trace of the  $D_Z$  tensor (which is already averaged with respect to the angle of the crystal axes relative to  $H_0$ ), is 7/5 times the value (35'). This is the average appropriate for theories of diffusion-limited relaxation by paramagnetic impurities in insulators.

The sum  $\sum_{ij} r_{ij}^{-4}$  has been evaluated by us for the bcc lattice, and is  $22.6/b^4$ , where  $b$  is the nearest-neighbor distance. The slow convergence of this sum means that the variation of (35') with respect to crystal axes will not be too great and may come from the variation of  $\langle \Delta\omega^2 \rangle^{1/2}$  as much as from the numerator sum.

If the perturbation-theory result (i.e., Eq. 35, with  $B_{ik} = A_{ik}$ ) is applied to the solid-He<sup>3</sup> problem, the predicted  $D_Z$  is approximately  $\sqrt{2}$  larger than the exact moment-calculation prediction, thereby worsening the agreement with experiment. Perturbation theory should be less applicable to this case since the off-diagonal and diagonal parts of the interaction are more nearly the same.

#### *Effect of Moderate Random Quadrupole Interaction*

Cubic crystals frequently contain sufficient impurities that virtually all nuclei feel an electric quadrupolar interaction, due to the strain set up by the impurities, which is larger than the dipolar interaction. This will change the spacings of the nuclear spin levels and thus eliminate many of the resonances between neighbors which permit them to mutually flip, as is needed in spin diffusion.

If the quadrupolar interaction is not too large, then the spacing between the  $m_s = +\frac{1}{2}$  and  $-\frac{1}{2}$  levels is unchanged for all spins, and transitions between these levels can still contribute to spin diffusion. In this section we assume that these are the only flip-flop transitions which are important in spin diffusion. This will be true only if the quadrupole interaction is strongly varying from spin to spin, and may not be a correct assumption if the interaction comes from a low density of point or line interactions, for example.<sup>20,21</sup>

To define the problem further we need to consider whether the  $|m_s| > \frac{1}{2}$  levels play any role at all in the problem. If the quadrupolar interaction were large enough, a spin in one of these levels would find no other spins reasonably close and resonant with it, and the spin would remain in that level until removed by lattice relaxation. We believe, however, that in many cases the quadrupole interaction will be small enough to permit

a spin in such a level to be moved out in a time comparable with the spin-diffusion time  $(D_Z k^2)^{-1}$ , by means of multiple spin flips like those proposed by Bloembergen *et al.*<sup>22</sup> In other words, we assume that the local spin temperature of the  $|m_s| > \frac{1}{2}$  part of the system is maintained the same as that of the  $|m_s| = \frac{1}{2}$  system, but diffusion is only by the latter. Thus, the diffusion coefficient is much smaller in this case. The  $|m_s| > \frac{1}{2}$  levels contribute most of the heat capacity of the system.

There are two ways to proceed: The easiest is via perturbation theory, comparing the sum of flip-flop transition probabilities for this case with the sum of probabilities for the many more cases allowed in the pure dipolar case. The second is to use for formalism of this paper, truncating  $S_{jx}$  and  $S_{jy}$  to include only the  $\pm\frac{1}{2}$  matrix elements.<sup>20</sup> The ratio  $M_4/M_2$  is easy to calculate if it is assumed that  $B_{jk}$  is much greater than  $A_{jk}$ , as in perturbation theory, because  $M_4/M_2$  is then unchanged from its perturbation value for the pure dipolar case. The result by either method is

$$D_{ZQ} = \frac{\{2[\frac{1}{4}(2S+1)]^2\}}{[\frac{1}{3}S(S+1)(2S+1)]^2} D_Z, \quad (36)$$

where  $D_{ZQ}$  is the diffusion coefficient in the presence of the quadrupolar interaction, and  $D_Z$  is that without. For  $S = \frac{7}{2}$ , the factor in front of  $D_Z$  is 0.0363.

In an earlier paper, one of us<sup>3</sup> expressed caution whether this theory is really applicable, because he believed that the slow variation of the fields coming from spins in the  $|m_s| > \frac{1}{2}$  levels would impede diffusion. For example, two spins in states  $|M_s| = \frac{1}{2}$  having the same local field might flip at some time, but if their local fields due to other spins did not change to randomize phases and make them nonresonant, they would flip back in a way not envisioned in perturbation theory.

We now doubt that this is a serious problem, for two reasons. First, the sum  $M_2$  of transition probabilities weighted against  $x_{ij}^2$  converges slowly, so that many spins are interacting importantly with a given spin, making for a more macroscopic system. Second, the theoretical second moment of the usual nuclear resonance line for this case,<sup>20</sup>  $S = \frac{7}{2}$ , is roughly twice that predicted if only the diagonal  $(B_{jk}I_{jz}I_{kz})$  part of  $\mathcal{H}$  is used to calculate  $\langle \Delta\omega^2 \rangle$ . Physically, this means that a spin in its  $m_s = \frac{1}{2}$  level feels a transverse, nearly resonant ac field due to precession of neighbors in their  $m_s = \pm\frac{1}{2}$  levels which is roughly the same size as the  $z$  field which it feels mostly from other neighbors in their  $|m_s| > \frac{1}{2}$  levels. The fraction  $2/(2S+1)$  of spins which are in  $\pm\frac{1}{2}$  levels thus form a system, with a strong transverse interaction, whose dynamics is not likely to be drastically affected by the comparable interaction with the rest of the system.

<sup>20</sup> This is the "semilike" case of K. Kambe and J. F. Ollom, J. Phys. Soc. Japan 11, 50 (1956).

<sup>21</sup> See also A. Abragam, *Nuclear Magnetism* (Oxford University Press, New York, 1961), p. 130.

<sup>22</sup> N. Bloembergen, S. Shapiro, J. A. Artman, and P. Pershan, Phys. Rev. 114, 445 (1959).

For  $S=\frac{7}{2}$  the result can be written

$$D_{ZQ} = 0.012\gamma^2\hbar^4 \sum_j r_{ij}^{-4} / \langle \Delta\omega^2 \rangle^{1/2}, \quad (37)$$

where we should emphasize that  $\langle \Delta\omega^2 \rangle$  is the Van Vleck second moment calculated assuming no quadrupolar interaction. For vanadium, we take  $\langle \Delta\omega^2 \rangle^{1/2}$  as  $2.42 \times 10^4 \text{ sec}^{-1}$ , and use the value for the sum given in Sec. III with nearest-neighbor distance 2.63 Å, obtaining  $D_{ZQ} = 5 \times 10^{-14} \text{ cm}^2/\text{sec}$ . From an experiment<sup>3</sup> on type-II superconducting vanadium we obtained 4.6 and  $7.7 \times 10^{-14} \text{ cm}^2/\text{sec}$  in different runs.

### V. SPIN DIFFUSION IN A MACROSCOPICALLY INHOMOGENEOUS FIELD

In this section, we point out briefly some features of diffusion of magnetization when there is a field gradient small enough that neighboring spins are in essentially the same magnetic field, but the two ends of the sample are in a very different field. We doubt whether these phenomena are of much importance in real systems. Some of the same considerations may be important in spectral diffusion.

Suppose we start with uniform magnetization and uniform field, and apply a field gradient. We expect that the system will tend toward a uniform spin temperature, via diffusion, with local magnetization proportional to local field.

But after diffusion has occurred, the average magnetic energy (space integral of  $-\mathbf{M} \cdot \mathbf{H}$ ) has decreased. The only place this energy can go is into spin-spin energy. This cannot go on long. Soon the spin-spin temperature would become negative.

The analysis of the problem is like that of cross relaxation of two overlapping resonances.<sup>23</sup> The Hamiltonian can be divided into two commuting parts. One part is the Hamiltonian of interaction with a uniform field equal to the average field. The other part contains the inhomogeneous part of the field (whose average is zero) plus the spin-spin interaction. The two subsystems of the second part of  $\mathcal{H}$  will tend toward equilibrium, and this means that diffusion will stop when  $(H-H_0)/(M-M_0)$  equals the temperature of the spin-spin part of the Hamiltonian divided by Curie's constant, where  $H_0$  and  $M_0$  are the average values of  $H$  and  $M$ .

Conversely, we can ask what happens if we prepare a crystal with a negative spin-spin temperature, then

put it in an inhomogeneous field. Spin diffusion will then proceed in the direction opposite to one's naive expectation, and the spin-spin temperature increases toward a high-negative temperature. By monitoring the increase of spin-spin temperature the diffusion coefficient could be measured.

The time constant for this degradation of spin-spin energy would be equal to  $D_Z$  times the field gradient squared divided by the mean-square local field in the rotating frame.<sup>24</sup> Using the estimate of Lowe and Gade,<sup>11</sup>  $D_Z = 3.5 \times 10^{-12} \text{ cm}^2/\text{sec}$ , and assuming a field gradient of 10 kG/cm, the time would be around  $\frac{1}{2}$  h. The main problem is to find a sample with such a long lattice relaxation time for spin-spin energy.

In a ferromagnet, the nuclear spin-diffusion coefficient is predicted to be huge by this theory because of the long range of the Suhl-Nakamura interaction between nuclei. If this prediction is correct, then the effects discussed here may be important and observable because of the inhomogeneous broadening typical for NMR in ferromagnets.

### VI. CONCLUSION

The most striking result of this calculation is the good agreement with the measured diffusion coefficients in He<sup>3</sup>. As emphasized by Bennett and Martin,<sup>14</sup> the diffusion process involves many collisions, whereas the present calculations are limited to three-spin interactions (for  $D_Z$ ) at most. The success of the calculation and the success of a related calculation<sup>25</sup> for spin relaxation indicate that the higher moments involved are related to the lowest moments in a simple way. It would be interesting to study the statistical topology of the diagrams representing terms of high moments, and the algebra of their contribution to the moments, to understand why this is so.<sup>15,26,27</sup> It would also be easy to calculate  $M_6$  (for  $D_Z$ ) and the corresponding moment which enters into spin-spin relaxation, to check the validity of the Gaussian approximation.

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<sup>24</sup> Reference 21, p. 547.

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