PHYSICAL REVIEW B VOLUME 2, NUMBER 11 1 DECEMBER 1970

Modified Linear-Response Method for Obtaining the Spin-Diffusion Constant of a Rigid Dipole System*

J. I. KAPLAN

Columbus Laboratories, Battelle Memorial Institute, 505 King Avenue, Columbus, Ohio 43201

(Received 13 April 1970)

The spin-diffusion constant D is obtained for a lattice of spin-$\frac{1}{2}$ particles with dipole-dipole coupling. The method of calculation is to create an equilibrium state with a nonuniform magnetization which is then allowed to relax after removal of the small inhomogeneous applied magnetic field. Comparison of the relaxation as calculated from a microscopic and macroscopic point of view defines D.

INTRODUCTION

There have been a number of calculations[1] for a lattice of dipole-dipole coupled $\frac{1}{2}$ spins of the spin-diffusion constant which appears in the nuclear Bloch equation,

$$\dot{M}_z(r_q) = D_q(\partial^2 M_z/\partial r_q^2), \tag{1}$$

where r_q is defined as $\mathbf{r}\cdot\mathbf{q}/|q|$. The excuse for another derivation of D_q is that the previous derivations are either quite complex and depend on approximations whose validity is not easily assessed or based on order-of-magnitude considerations. The linear response method[2] has been simply and successfully applied to calculations of D_q for an electron gas[3] so it seemed an appropriate method for obtaining D_q for spins on a lattice. A straightforward application of the usual method led to difficulties. Instead we use the linear inhomogeneous field only to prepare our state. The relaxation of our system from a macroscopic and microscopic point of view will be shown to define D_q.

CALCULATION

Using a macroscopic description one has for $t=0$ the magnetization

$$M_z(0, r_q) = M_{z0} + \bar{M}_z(0)\,\sin\mathbf{q}\cdot\mathbf{r}, \tag{2}$$

which for $t>0$ we assume obeys the diffusion equation

$$\dot{M}_z(t, r_q) = D_q(\partial^2 M_z/\partial r_q^2). \tag{3}$$

Substituting Eq. (2) for $t>0$ into Eq. (3) one obtains

$$\bar{M}_z(t) = \bar{M}_z(0)\,\exp(-\alpha t), \tag{4}$$

$$\alpha = q^2 D_q. \tag{5}$$

From a microscopic point of view one has for $t<0$

$$\langle I_i^z\rangle = \mathrm{Tr}\, I_i^z \rho(0), \tag{6}$$

where $\rho(0)$ is the density matrix for the inhomogeneous equilibrium state

$$\rho(0) = \exp[-(H+H^1)\beta]/\mathrm{Tr}\,\exp[-(H+H^1)\beta], \tag{7}$$

where[4]

$$H = -\omega_0 \sum I_i^z + \sum_{i>j} B_{ij} I_i^z I_j^z + \sum_{i>j} \tfrac{1}{2}(A_{ij})(I_i^+ I_j^- + I_i^- I_j^+) = H_0 + H_1 + H_2, \tag{8}$$

$$H^1 = -U \sum_i I_i^z \sin\mathbf{q}\cdot\mathbf{r}_i. \tag{9}$$

Substituting Eq. (7) into Eq. (6) and using the expansion[5]

$$\rho(0) = [\mathscr{I} - (H+H^1)\beta]/\mathrm{Tr}\mathscr{I}, \tag{10}$$

valid for all usual laboratory situations, one obtains

$$\langle I_i^z\rangle = \tfrac{1}{3}[\beta I(I+1)](\omega_0 + U\sin\mathbf{q}\cdot\mathbf{r}_i). \tag{11}$$

Equation (11) is to be identified with the macroscopic equation (2).

For $t>0$ one has

$$\langle \dot{I}_i^z\rangle = \mathrm{Tr}\, I_i^z\dot{\rho} = i\,\mathrm{Tr}\rho[H, I_i^z] = i\,\mathrm{Tr}\rho[H_2, I_i^z], \tag{12}$$

using the relations

$$\dot{\rho} = i[\rho, H], \tag{13}$$

$$\tilde{H} = H_0 + H_1, \qquad [\tilde{H}, I_i^z] = 0. \tag{14}$$

By solving Eq. (13) with the boundary condition that at $t=0$

$$\rho = \rho(0), \tag{15}$$

we obtain

$$\rho(t) = \exp(-i\tilde{H}t)\rho(0)\exp(i\tilde{H}t) + i\int_0^t \exp[-i(t-t')\tilde{H}][\rho(t'), H_2]\exp[i(t-t')\tilde{H}]dt'. \tag{16}$$

Equation (16) is then substituted into Eq. (12) to obtain

$$\langle \dot{I}_i^z\rangle = i\,\mathrm{Tr}\,\exp(-i\tilde{H}t)\rho(0)\exp(i\tilde{H}t)[H_2, I_i^z] + (i)^2\int_0^t \mathrm{Tr}\rho(t-u)[H_2,[H_2(u), I_i^z]]du, \tag{17}$$

where

$$H_2(u) = \exp(i\tilde{H}u)H_2\exp(-i\tilde{H}u).$$

The first term on the right-hand side can be shown to be zero. In the second term of the right-hand side, which is already of second order in H_2, we substitute $\rho(t-u)$, correct to zero order in H_2. From Eqs. (16) and (14) this is seen to be

$$\rho(t-u)=\rho(0). \tag{18}$$

Lowe and Gade[1] expand

$$[H_2, [H_2(u), I_i^z]] \tag{19}$$

as their Eqs. (31)–(33). Substituting Eq. (18) and Lowe and Gade's Eqs. (31)–(33) into Eq. (17) one obtains

$$\langle \dot{I}_i^z\rangle = 2(i)^2(-\beta)U \sum_{k(k\neq i)} A_{ik}^2 (\sin\mathbf{q}\cdot\mathbf{r}_i - \sin\mathbf{q}\cdot\mathbf{r}_k) \times \int_0^t \tilde{L}_{ik}(u)\,du[\tfrac{1}{3}I(I+1)], \tag{20}$$

where

$$\tilde{L}_{ik}(u)=\prod_{j\neq i,k}[\cos(B_{ij}-B_{kj})u]. \tag{21}$$

The integral

$$\int_0^t \tilde{L}(u)\,du = \int_0^t \exp[\ln\tilde{L}(u)]du = \int_0^t \exp\{\sum_{j\neq(i,k)} \ln[\cos(B_{ij}-B_{kj})u]\}du \tag{22}$$

is in a form suitable for the method of steepest descent.[6] One then obtains, assuming t lies above the region where $\tilde{L}(u)$ is appreciable,

$$F_{ik}=\int_0^t \exp[\ln\tilde{L}(u)] \simeq \int_0^\infty \exp\{\ln\tilde{L}(0)+\tfrac{1}{2}X^2[\tilde{L}''(0)/\tilde{L}(0)]\}dX = \tfrac{1}{2}(\pi/\Delta_{ik})^{1/2}, \tag{23}$$

where

$$\Delta_{ik}=\tfrac{1}{2}\sum_{j\neq(i,k)}(B_{ij}-B_{kj})^2. \tag{24}$$

Identifying Eq. (20) with the macroscopic $\dot{M}_z$ [Eq. (3)] one obtains

$$-q^2D_{\mathrm{q}}=2(i)^2(-\beta)U\sum_{k(k\neq i)} A_{ik}^2F_{ik}[\tfrac{1}{3}I(I+1)][\sin\mathbf{q}\cdot\mathbf{r}_i-\sin\mathbf{q}\cdot\mathbf{r}_k]/\{-\beta U\sin\mathbf{q}\cdot\mathbf{r}_i[\tfrac{1}{3}I(I+1)]\}. \tag{25}$$

Thus for long wavelengths one identifies

$$D_{\mathrm{q}}=\sum_{k(k=i)} A_{ik}^2F_{ik}\left(\frac{(\mathbf{r}_k-\mathbf{r}_i)\cdot\mathbf{q}}{|q|}\right)^2, \tag{26}$$

which is equivalent to Lowe and Gade's Eq. (61) for D_{q} evaluated to order H_2^2. D_{q} calculated to terms higher order in H_2 can be obtained straightforwardly, but laboriously, by solving Eq. (16) by iteration as a power series in $H_2(t)$ and then substituting into Eq. (17) and taking the limit $t\rightarrow\infty$. The author believes that D_{q} to third order in H_2 found this way would agree in a qualitative but not quantitative way with the results obtained by Lowe and Gade.

In Eqs. (1) and (3) we have avoided including the spin-lattice relaxation-time interaction. This is not necessary, but it does make the algebra simpler. Including the spin relaxation time T_1 will only modify our results by replacing Eq. (23) by

$$\int_0^t \tilde{L}(u)\exp(-u/T_1)\,du \simeq \tfrac{1}{2}(\pi/\Delta)^{1/2}\exp(\epsilon^2)[1-\Phi(\epsilon)], \tag{27}$$

where

$$\epsilon^2=(4\Delta T_1^2)^{-1},$$

$$\Phi(\epsilon)=(2\pi^{1/2})\int_0^\epsilon e^{-Z^2}\,dZ.$$

For the usual spin system $\epsilon\ll 1$ and Eq. (29) will be independent of T_1.

CONCLUSION

We have obtained D_{q} correct to second order in H_2. This is sufficient for systems whose time variation is slight on the scale of T_2, which is the order of the decay time of $\tilde{L}(u)$. The present results to this order agree with Lowe and Gade.[1] The method also gives an unambiguous prescription for obtaining D_{q} to any order in H_2, and with a simple modification, the spin-lattice dependence of D_{q} can also be included.

* Work supported by the Office of Naval Research, under Contract No. N00014-69-C-0218. Part of work was done during the summer 1969 at the Aspen Center of Physics, Aspen, Colo.

[1] N. Bloembergen, Physica **15**, 386 (1949); A. G. Redfield, Phys. Rev. **116**, 315 (1959); L. L. Buishvili and D. N. Zubarev, Fiz. Tverd. Tela **7**, 722 (1965) [Soviet Phys. Solid State **7**, 580 (1965)]; I. J. Lowe and S. Gade, Phys. Rev. **156**, 817 (1967); P. Borckmans and D. Walgraef, *ibid.* **167**, 282 (1968).

[2] H. Ehrenreich and M. H. Cohen, Phys. Rev. **115**, 786 (1959).

[3] J. I. Kaplan, Phys. Rev. **143**, 351 (1966); G. D. Gaspari, *ibid.* **151**, 215 (1966); P. M. Platzman and P. A. Wolff, *ibid.* **18**, 280 (1967).

[4] C. P. Slichter, *Principles of Magnetic Resonance* (Harper and Row, New York, 1963), p. 46.

[5] Reference 4, Appendix E.

[6] J. Mathews and J. L. Walker, *Mathematical Methods of Physics* (Benjamin, New York, 1964), p. 78.