

## Spin diffusion in NMR in solids

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The spin-flip diffusion equation for the local magnetization in solids is derived using Mori's equation of motion with the emphasis on the types of approximations involved. The spin-flip diffusion coefficient is expressed in terms of the local dipolar field. Comparison with other theories is also given. The effect of spin diffusion on nuclear magnetic resonance in disordered solids with a spatial distribution of resonance frequency  $\omega(\vec{r})$  and longitudinal spin-relaxation time  $T_1(\vec{r})$  has been investigated in the limits of (a) rapid diffusion:  $Dl^{-2} \gg |\Delta A|$ , and (b) slow diffusion:  $Dl^{-2} \ll |A(\vec{r})|$  and  $|\Delta A|$ .  $D$  is the spin diffusion coefficient,  $A(\vec{r}) = -i\omega(\vec{r})$  or  $T_1(\vec{r})^{-1}$ ,  $|\Delta A|$  is the maximal variation in  $A(\vec{r})$ , and  $l$  is the average distance between extrema in  $A(\vec{r})$ . In the rapid diffusion limit, the case of  $A(\vec{r}) = T_1(\vec{r})^{-1}$  and  $A(\vec{r}) = -i\omega(\vec{r})$  can be studied under the same treatment based on cumulant expansion method or second-order perturbation theory. Both yield the same results. The line shape is found to be a motionally narrowed Lorentzian whose width is determined by the spatial correlation of  $\omega(\vec{r})$ ; in comparison with the result in the limit of  $D \rightarrow \infty$ , the longitudinal relaxation time of the sample as a whole is lengthened. The difference is determined by the spatial correlation of  $1/T_1(\vec{r})$ . On the other hand in the slow diffusion limit, the case of  $A(\vec{r}) = T_1(\vec{r})^{-1}$  and  $A(\vec{r}) = -i\omega(\vec{r})$  have to be studied separately. Here selective summation of a perturbation expansion to an infinite order is involved. The procedure by which such expansion is summed depends on whether  $A(\vec{r})$  is real [ $A(\vec{r}) = T_1(\vec{r})^{-1}$ ] or imaginary [ $A(\vec{r}) = -i\omega(\vec{r})$ ]. The individual absorption line is now broadened by spin diffusion. In both limits, analytic expressions of the line broadening and the lengthening of the relaxation time are given. The differences between these results and those of  $D = 0$  and  $\infty$  yield information about the spatial distribution of  $A(\vec{r})$ .

## I. INTRODUCTION

Spin diffusion has played an important role in the understanding of various nuclear-magnetic-resonance (NMR) phenomena in disordered solids. Bloembergen<sup>1</sup> pointed out more than three decades ago that the rather short longitudinal spin-relaxation time  $T_1$  in solids with paramagnetic impurities could be explained by the spatial diffusion of the longitudinal spin magnetization  $M_Z$  from distant spins to the paramagnetic sites where rapid relaxations to the lattice are possible. Such a spatial transport of magnetization can be brought about by mutual spin flip via the strong dipole-dipole interactions among nuclear spins; no physical translations of spins are involved. Similarly, the rapid spin-lattice relaxation in polyethylene<sup>2</sup> at low temperature was explained in terms of the diffusion of  $M_Z$  from the rigid methylene protons to the mobile methyl protons at the chain ends. Spin diffusion between different phases in polymer systems<sup>3-5</sup> has also been observed recently.

On the other hand, nuclear spins may undergo self-diffusion in which a spin jumps physically from one site to another. If a spin experiences different Larmor precessions at different sites, self-diffusion

will lead to the dephasing<sup>6-9</sup> of the spin precession and consequently the decaying of the transverse magnetization  $M_T$ .

In general, different sites in a disordered solid can have different environments in which a spin can relax with different  $T_1$  and/or precess with different Larmor frequency  $\omega$ . Spin diffusion induced by either physical translation or mutual spin flip allows spins to sample such differences. In a broad sense, spin diffusion represents a motional averaging process.

The traditional approach to the spin-diffusion problem is to set up a diffusion equation for  $M_\alpha(\vec{r}, t)$ .

$$\dot{M}_\alpha(\vec{r}, t) = D \nabla^2 M_\alpha(\vec{r}, t) - A_\alpha(\vec{r}) M_\alpha(\vec{r}, t) \quad (1)$$

$$\alpha = Z, T$$

Then the differential equation is solved according to a set of boundary conditions<sup>1,10-13</sup> determined by the properties of the system in question. Thus one needs to know *a priori* the spatial variation of the scalar field  $A_\alpha(\vec{r})$ , where

$$A_\alpha(\vec{r}) = \begin{cases} T_1(\vec{r})^{-1}, & \alpha = Z \\ -i\omega(\vec{r}), & \alpha = T \end{cases}$$

For a complicated  $A_\alpha(\bar{\tau})$  even numerical calculations are rather involved, let alone analytic solutions.

However, it is obvious that in the limit of  $D \rightarrow \infty$ , where  $D$  is the spin-diffusion coefficient, each spin has the opportunity to sample all the possible values of  $A_\alpha(\bar{\tau})$  within an experimental time scale. The net effect is that each spin sees only  $\langle\langle A_\alpha(\bar{\tau}) \rangle\rangle$ , the spatial average of  $A_\alpha(\bar{\tau})$ . The time evolution of the average magnetization per unit volume,  $p_\alpha(t)$ , which is the observed quantity, is then given by a single exponential decay,

$$p_\alpha(t) = p_0 \exp[-\langle\langle A_\alpha(\bar{\tau}) \rangle\rangle t] . \quad (2)$$

On the other hand, in the limit of  $D \rightarrow 0$ , a spin at site  $\bar{\tau}_n$  sees only  $A_\alpha(\bar{\tau} = \bar{\tau}_n)$  and nothing else. Now  $p_\alpha(t)$  must be represented by a distribution of exponential terms

$$p_\alpha(t) = p_0 \langle\langle \exp[-A_\alpha(\bar{\tau})t] \rangle\rangle , \quad (3a)$$

which is equivalent to

$$p_\alpha(t) = p_0 \int dA_\alpha I(A_\alpha) \exp(-A_\alpha t) , \quad (3b)$$

where  $I(A_\alpha)$  is the normalized distribution of  $A_\alpha(\bar{\tau})$  in the system and is independent of  $\bar{\tau}$ .

In Eqs. (2), (3a), and (3b), we have used the simplification of  $M_\alpha(\bar{\tau}, t=0) = p_0$  for all  $\bar{\tau}$ .

In this paper, we shall show that corrections to the above limiting cases can be evaluated analytically.

Indeed, the effects of spin diffusion on NMR are amenable to detailed analysis in two general cases:

(1) rapid diffusion where  $D/l^2 \gg |\Delta A_\alpha|$ , and (2) slow diffusion where  $D/l^2 \ll |A_\alpha(\bar{\tau})|$  and  $|\Delta A_\alpha|$ .  $\Delta A_\alpha$  is the maximal variation in  $A_\alpha(\bar{\tau})$ , i.e.,  $\Delta A_\alpha = A_\alpha^{\max} - A_\alpha^{\min}$ , and  $l$  is the average distance between  $A_\alpha^{\max}$  and  $A_\alpha^{\min}$  in the system.

We shall first derive the spin-flip diffusion equation for the case of  $A_\alpha(\bar{\tau}) = T_1(\bar{\tau})^{-1}$  in Sec. II. Though similar equations have been derived by others,<sup>14,15</sup> our derivation based on Mori's equation of motion<sup>16</sup> is much simpler, thereby permitting us to focus our attention on the kinds of approximations involved. The spin-flip diffusion coefficient will be expressed in terms of the local dipolar field. Comparison with other theories is also discussed. The results for the rapid-diffusion and slow-diffusion cases are presented, respectively, in Secs. III and IV. In the former, since a spin has ample opportunity to experience the different  $A_\alpha(\bar{\tau})$  at different sites, the time evolution of  $p_\alpha(t)$  must be determined as shall be shown below, by the spatial correlation of  $A_\alpha(\bar{\tau})$ . In contrast,  $[\nabla A_\alpha(\bar{\tau})]^2$  and  $\nabla^2 A_\alpha(\bar{\tau})$  suffice for the latter case, since the time evolutions of a spin at a site  $\bar{\tau}_n$  depends mainly on the local variation of  $A_\alpha(\bar{\tau})$  at  $\bar{\tau}_n$ . Our treatment of the rapid diffusion is based on cumulant expansion method and second-order perturbation theory. In the slow-diffusion case, selective summation of a perturbation expansion to infinite order is involved.

## II. SPIN-FLIP DIFFUSION EQUATION

We are interested in the time evolution of the longitudinal magnetization  $M_Z(\bar{\tau}_n, t)$  at site  $\bar{\tau}_n$  and time  $t$  in a lattice of spins. Since dipolar interactions couple spins among each other, the evolution of each spin depends on its neighbors. The treatment of such a many-body problem can be handled conveniently by Mori's equation of motion.<sup>16</sup>

The total Hamiltonian for our system may be written as

$$\mathcal{H} = \mathcal{H}_L + \mathcal{H}_D + \mathcal{H}_Z , \quad (4)$$

where  $H_L$  is the lattice Hamiltonian and  $H_Z$  is the Zeeman energy due to the external static magnetic field  $\bar{H}_0$

$$\mathcal{H}_Z = \sum_n \hbar \omega_n S_{nz} , \quad (5)$$

which is much larger than the dipolar interactions  $H_D$ . We can decompose<sup>17</sup>  $\mathcal{H}_D$  into the secular and nonsecular components

$$\begin{aligned} \mathcal{H}_D &= \sum_{i=-2}^2 \mathcal{H}_D^i , \\ \mathcal{H}_D^0 &= \frac{1}{2} \sum_{\langle nm \rangle} \lambda_{nm}^0 \left( \frac{S_{n+} S_{m-} + S_{n-} S_{m+}}{4} - S_{nz} S_{mz} \right) , \\ \mathcal{H}_D^1 &= \frac{1}{2} \sum_{\langle nm \rangle} \lambda_{nm}^1 (S_{nz} S_{m+} + S_{n+} S_{mz}) , \\ \mathcal{H}_D^2 &= \frac{1}{2} \sum_{\langle nm \rangle} \lambda_{nm}^2 S_{n+} S_{m+} , \\ \mathcal{H}_D^{-1} &= (\mathcal{H}_D^1)^* , \end{aligned} \quad (6)$$

and

$$\mathcal{H}_D^{-2} = (\mathcal{H}_D^2)^* ,$$

where

$$\begin{aligned} \lambda_{nm}^0 &= (3 \cos^2 \theta_{nm} - 1) \hbar^2 \gamma^2 / r_{nm}^3 , \\ \lambda_{nm}^1 &= -\frac{3}{2} \sin \theta_{nm} \cos \theta_{nm} e^{-i\phi_{nm}} \hbar^2 \gamma^2 / r_{nm}^3 , \\ \lambda_{nm}^2 &= -\frac{3}{4} \sin^2 \theta_{nm} e^{-i2\phi_{nm}} \hbar^2 \gamma^2 / r_{nm}^3 . \end{aligned} \quad (7)$$

For simplicity, the summation  $\langle nm \rangle$  can be restricted to nearest neighbors only. In Eq. (7),  $\theta_{nm}$  and  $\phi_{nm}$  are the polar and azimuthal angles relating the vector  $\bar{r}_{nm}$  connecting the spins at site  $\bar{\tau}_n$  and  $\bar{\tau}_m$  to the laboratory frame defined by the external field  $\bar{H}_0$ .  $\gamma$  is the gyromagnetic ratio of the spins and

$$r_{nm} = |\bar{\tau}_n - \bar{\tau}_m| .$$

$M_Z(\bar{\tau}_n, t)$  measured with respect to its equilibrium value  $M_Z(\bar{\tau}_n, t \rightarrow \infty)$  is given by the difference between the thermal averages of  $S_{nz}$  over the instantaneous ensemble at time  $t$  and the equilibrium ensemble. Using Mori's equation of motion and the linear response approximation,<sup>18</sup> we obtain

$$\dot{M}_Z(\bar{\tau}_n, t) = - \sum_m \int_0^t d\tau \frac{\langle (U(t-\tau)[\mathcal{J}C_D, S_{nz}])[S_{mz}, \mathcal{J}C_D] \rangle}{\langle S_{mz}^2 \rangle} M_Z(\bar{\tau}_m, \tau) \quad (8)$$

where  $\langle \dots \rangle$  denotes the equilibrium thermal averaging.  $U(t)$  in Eq. (8) is the well-known modified time evolution operator; it is sufficient to mention that it involves the projection operator  $P$  defined as

$$PX \equiv \sum_n \langle XS_{nz} \rangle \langle S_{nz}^2 \rangle^{-1} S_{nz}$$

for an arbitrary operator  $X$ .

Denoting  $S_{n+}$ ,  $S_{nz}$ , and  $S_{n-}$  by  $S_n^\beta$  with  $\beta = 1, 0,$  and  $-1$ , respectively, a typical term of the memory kernel in Eq. (8) is of the form

$$\langle \tilde{\lambda}_{nm}^i(t) \lambda_{n'm'}^{-i'} \tilde{S}_n^\beta(t) \tilde{S}_m^\gamma(t) S_n^{-\beta'} S_m^{-\gamma'} \rangle$$

with  $\beta + \gamma = i$ ,  $\beta' + \gamma' = i'$ ,  $\tilde{S}_n^\beta(t) \equiv U(t)S_n^\beta$ , and  $\tilde{\lambda}_{nm}^i(t) \equiv U(t)\lambda_{nm}^i$ . The usual approximations for evaluating such a term are to take the thermal averaging over the lattice and spin variables independently and to apply the random-phase approximation

$$\begin{aligned} \langle \tilde{S}_n^\beta(t) \tilde{S}_m^\gamma(t) S_n^{-\beta'} S_m^{-\gamma'} \rangle \\ \simeq \langle \tilde{S}_n^\beta(t) S_n^{-\beta} \rangle \langle \tilde{S}_m^\gamma(t) S_m^{-\gamma} \rangle \\ \times (\delta_{nn'} \delta_{mm'} \delta_{\beta\beta'} \delta_{\gamma\gamma'} + \delta_{nm'} \delta_{mn'} \delta_{\beta\gamma'} \delta_{\gamma\beta'}) \quad (9) \end{aligned}$$

Since the projection operator  $P$  has negligible effects on the lattice variables except at the lowest temperatures,  $\tilde{\lambda}_{nm}^i(t)$  can be replaced by  $\lambda_{nm}^i(t)$ . Also

$\langle \tilde{S}_n^\beta(t) S_n^{-\beta} \rangle$  may be written as

$$\langle \tilde{S}_n^\beta S_n^{-\beta} \rangle \equiv \langle S_n^\beta S_n^{-\beta} \rangle g_\beta(t) \exp i\beta\omega_n t \quad (10)$$

where now the time dependence of  $g_\beta(t)$  [ $g_\beta(t) = g_{-\beta}(t)$ ] is primarily dictated by  $\mathcal{J}C_D$ . Substituting Eqs. (9) and (10) into the memory kernel leads to

$$\begin{aligned} \langle (U(t)[\mathcal{J}C_D, S_{nz}])[S_{mz}, \mathcal{J}C_D] \rangle / \langle S_{mz}^2 \rangle \\ = \sum_i \langle (U(t)[\mathcal{J}C_D, S_{nz}])[S_{mz}, \mathcal{J}C_D^{-i}] \rangle / \langle S_{mz}^2 \rangle \\ = \left[ \delta_{nm} \sum_{\langle m' \rangle} L_{nm'}^{(0)}(t) - L_{nm}^{(0)}(t) \right] + \delta_{nm} \sum_{\langle m' \rangle} L_{nm'}^{(1)}(t) \\ + \left[ \delta_{nm} \sum_{\langle m' \rangle} L_{nm'}^{(2)}(t) + L_{nm}^{(2)}(t) \right] \quad (11) \end{aligned}$$

where

$$L_{nm}^{(0)}(t) = \frac{1}{6} S(S+1) \langle \lambda_{nm}^0(t) \lambda_{nm}^0 \rangle g_1^2(t) \cos(\omega_n - \omega_m)t \quad (12)$$

$$L_{nm}^{(1)}(t) = \frac{4}{3} S(S+1) \langle \lambda_{nm}^1(t) \lambda_{nm}^{-1} \rangle g_1(t) g_0(t) \cos\omega_n t \quad (13)$$

$$L_{nm}^{(2)}(t) = \frac{8}{3} S(S+1) \langle \lambda_{nm}^2(t) \lambda_{nm}^{-2} \rangle g_1^2(t) \cos(\omega_n + \omega_m)t \quad (14)$$

The summation  $\langle m' \rangle$  is restricted to nearest neighbors of the site  $\bar{\tau}_n$  only. Then from Eq. (8), one finds

$$\begin{aligned} \dot{M}_Z(\bar{\tau}_n, t) = \int_0^t d\tau \sum_{\langle m \rangle} L_{nm}^{(0)}(t-\tau) [M_Z(\bar{\tau}_m, \tau) - M_Z(\bar{\tau}_n, \tau)] - \int_0^t d\tau \left[ \sum_{\langle m \rangle} L_{nm}^{(1)}(t-\tau) \right] M_Z(\bar{\tau}_n, \tau) d\tau \\ - \int_0^t d\tau \sum_{\langle m \rangle} L_{nm}^{(2)}(t-\tau) [M_Z(\bar{\tau}_m, \tau) + M_Z(\bar{\tau}_n, \tau)] \quad (15) \end{aligned}$$

Whenever the difference between  $M_Z(\bar{\tau}_n, t)$  and  $M_Z(\bar{\tau}_m, t)$  at the nearest-neighboring sites  $\bar{\tau}_n$  and  $\bar{\tau}_m$  is sufficiently small, the last term on the right-hand side of Eq. (15) becomes

$$\int_0^t d\tau 2 \sum_{\langle m \rangle} L_{nm}^{(2)}(t-\tau) M_Z(\bar{\tau}_n, \tau) \quad (16)$$

In the continuum limit, Eq. (15) makes the transition to a differential equation

$$\dot{M}_Z(\bar{\tau}, t) = \int_0^t d\tau \bar{\nabla} \cdot \frac{a_0^2}{2} L^{(0)}(\bar{\tau}, t-\tau) \cdot \bar{\nabla} M_Z(\bar{\tau}, \tau) - \int_0^t d\tau [L^{(1)}(\bar{\tau}, t-\tau) + 2L^{(2)}(\bar{\tau}, t-\tau)] M_Z(\bar{\tau}, \tau) \quad (17)$$

with

$$\sum_{\langle m \rangle} L_{nm}^{(0)}(t) \rightarrow L^{(0)}(\bar{\tau}, t) \quad , \quad \sum_{\langle m \rangle} L_{nm}^{(1)}(t) \rightarrow L^{(1)}(\bar{\tau}, t) \quad ,$$

and

$$\sum_{\langle m \rangle} L_{nm}^{(2)}(t) \rightarrow L^{(2)}(\bar{r}, t) .$$

In Eq. (17), we have denoted the lattice constant by  $a_0$  and have also assumed that the environment around each site is isotropic. For an anisotropic solid, we have to replace  $(a_0^2/2)L^{(0)}(\bar{r}, t)$  by a dyadic  $\bar{\Gamma}^{(0)}(t)$  and the first term at the right-hand side of Eq. (17) by

$$\int_0^t \bar{\nabla} \cdot \bar{\Gamma}^{(0)}(\bar{r}, t - \tau) \cdot \bar{\nabla} M_Z(\bar{r}, \tau) d\tau .$$

The final transition to the spin-diffusion equation given by Eq. (1) involves the basic assumptions that  $M_Z(\bar{r}, t)$  and  $\nabla^2 M_Z(\bar{r}, t)$  decay in time much slower than  $L^{(i)}(\bar{r}, t)$ ,  $i = 0, 1, 2$  such that a Markoffian approximation<sup>19</sup> may be applied and that  $L^{(0)}(\bar{r}, t)$  is independent of  $\bar{r}$ . Hence one may write

$$\begin{aligned} \int_0^t d\tau \bar{\nabla} \cdot \frac{a_0^2}{2} L^{(0)}(\bar{r}, t - \tau) \cdot \bar{\nabla} M_Z(\bar{r}, \tau) \\ = \frac{a_0^2}{2} \int_0^t d\tau L^{(0)}(\tau) \nabla^2 M_Z(\bar{r}, t) \\ \simeq \frac{a_0^2}{2} \left( \int_0^\infty d\tau L^{(0)}(\tau) \right) \nabla^2 M_Z(\bar{r}, t) . \end{aligned}$$

The spin-diffusion coefficient  $D$  and the relaxation time  $T_1(\bar{r})$  in Eq. (1) for the case of spin-flip diffusion are then given by

$$D = \frac{a_0^2}{2} \int_0^\infty L^{(0)}(\tau) d\tau \quad (18)$$

and

$$T_1(\bar{r})^{-1} = \int_0^\infty L^{(1)}(\bar{r}, \tau) d\tau + \int_0^\infty 2L^{(2)}(\bar{r}, \tau) d\tau . \quad (19)$$

The Markoffian approximation is usually justified for the reason that the time evolution of  $g_0(t)$  and  $g_1(t)$  in Eqs. (12)–(14) are governed by  $\mathcal{H}_D$ . In solids, they decay in time of the order of  $T_2$  which is much shorter than the decay time of  $M_Z(\bar{r}, t)$  which is of the order of  $T_1$ . The very nature of the Markoffian approximation limits the validity of the spin-flip diffusion equation to  $t \gg T_2$ . In addition, it has been shown that Eq. (1) fails to satisfy certain thermodynamic sum rules.<sup>20</sup> This is a consequence of the Markoffian approximation. Neglecting the contributions of  $T_1(\bar{r})$  to Eq. (1) for a moment, we can see that the magnetization current  $\bar{J}(\bar{r}, t)$  defined by the continuity equation

$$\dot{M}_Z(\bar{r}, t) = -\bar{\nabla} \cdot \bar{J}(\bar{r}, t) , \quad (20)$$

becomes

$$\bar{J}(\bar{r}, t) = -D \bar{\nabla} M_Z(\bar{r}, t) , \quad (21)$$

which means that the current responds instantane-

ously to changes in the magnetization  $M_Z(\bar{r}, t)$ . Actually, there must be some lag in the response of  $\bar{J}(\bar{r}, t)$  to the changes in  $M_Z(\bar{r}, t)$  as indicated by the time convolution in Eq. (17). Explicitly, by combining Eqs. (20) and (17), we have

$$\bar{J}(\bar{r}, t) = - \int_0^t \frac{a_0^2}{2} L^{(0)}(\bar{r}, t - \tau) \bar{\nabla} M_Z(\bar{r}, \tau) d\tau . \quad (22)$$

The time derivative of  $J(\bar{r}, t)$  may be written as

$$\begin{aligned} \frac{\partial \bar{J}(\bar{r}, t)}{\partial t} &= - \frac{a_0^2}{2} L^{(0)}(\bar{r}, 0) \bar{\nabla} M_Z(\bar{r}, t) \\ &\quad - \frac{a_0^2}{2} \int_0^t \dot{L}^{(0)}(\bar{r}, t - \tau) M_Z(\bar{r}, \tau) d\tau \\ &\simeq -\tau_c^{-1} [D \bar{\nabla} M_Z(\bar{r}, t) + \bar{J}(\bar{r}, t)] . \quad (23) \end{aligned}$$

Thus the changes in  $\bar{J}(\bar{r}, t)$  depend not only on  $M_Z(\bar{r}, t)$  but also on its instantaneous value. The second equality in Eq. (23) follows from the approximation that there is a single relaxation time  $\tau_c$  in  $L^{(0)}(\bar{r}, t)$  such that we may write

$$\frac{a_0^2}{2} L^{(0)}(\bar{r}, 0) \simeq \frac{a_0^2}{2} \tau_c^{-1} \int_0^\infty L^{(0)}(\bar{r}, \tau) d\tau = D \tau_c^{-1}$$

and

$$\dot{L}^{(0)}(\bar{r}, t - \tau) \simeq -\tau_c^{-1} L^{(0)}(\bar{r}, t - \tau) .$$

Kadanoff and Martin have introduced Eq. (23) phenomenologically<sup>20</sup> and showed that the equation of motion of  $M_Z(\bar{r}, t)$  obtained by substituting Eq. (23) into the continuity equation indeed satisfies the thermodynamic sum rules violated by Eq. (1). The existence of a finite lag ( $\tau_c \neq 0$ ) has been important for the understanding of some low-temperature NMR experiments.<sup>21</sup>

Usually when  $r_{nm}$  between any adjacent sites  $\bar{r}_n$  and  $\bar{r}_m$  is more or less constant throughout the sample, the assumption of a  $\bar{r}$  independent  $D$  is justified. However one should note that we have retained the  $\bar{r}$  dependence in  $T_1(\bar{r})$ . A main source which may lead to a  $\bar{r}$  dependent  $T_1(\bar{r})$  and  $D$  is the existence of nonuniform and localized lattice motions. Such motions may affect  $\lambda_{nm}^i$  in Eqs. (12)–(14) by modulating its angular variables,  $\theta_{nm}$  and  $\phi_{nm}$ . These localized modulations may be quite different at different sites. What makes  $T_1(\bar{r})$  differ from  $D$  is that lattice motions are rather restricted in solids and that  $D$  is given by the time integral of Eq. (12) which involves  $\cos(\omega_n - \omega_m)t$ , whereas the time integrals in  $T_1(\bar{r})^{-1}$  involve  $\cos\omega_n t$  and  $\cos(\omega_n + \omega_m)t$ . Since a nonzero  $(\omega_n - \omega_m)$  is mainly due to a difference in chemical shielding which is much smaller than the decay rate ( $\sim T_2^{-1}$ ) of  $g_1(t)$ , unless there are large amplitude

and rapid motions (in comparison with  $T_2^{-1}$ ) in  $\lambda_{nm}^0(t)$ , the time integral in  $D$  is not affected. However it is quite a different situation for  $T_1(\bar{\tau})^{-1}$ . Here we have  $\omega_n \gg T_2^{-1}$ ; the time integrals in  $T_1(\bar{\tau})$  are highly sensitive to the spectral density<sup>17</sup> of  $\lambda_{nm}^i(t)$ ,  $i = 1, 2$  at the frequencies of  $\omega_n$  and  $(\omega_n + \omega_m) \approx 2\omega_n$ . In other words, even though lattice motions are of small amplitude, so long as  $\lambda_{nm}^i(t)$  has sufficient frequency components around  $\omega_n$  and  $2\omega_n$ ,  $T_1(\bar{\tau})^{-1}$  will be primarily determined by those components. Since it is entirely possible for different site to have different types of local motions, thus different spectral density for  $\lambda_{nm}^i(t)$ , we expect to have  $T_1(\bar{\tau})^{-1}$  depend on  $\bar{\tau}$ .

We conclude this section with the evaluation of the spin-flip diffusion coefficient given by Eq. (18). It has been shown that  $g_1(t)$  in Eq. (12) can be adequately described by a Gaussian decay,<sup>22</sup>

$$g_1(t) = \exp(-B^2 t^2) \quad (24)$$

with  $B$  approximately<sup>23</sup> given by

$$B^2 = \frac{5}{24} S(S+1) \sum_{\langle m \rangle} \langle \lambda_{nm}^0 \lambda_{nm}^0 \rangle \quad (25)$$

Evaluating the integral in Eq. (18), with  $(\omega_n - \omega_m) = 0$ , leads to

$$D = Ca_0^2 \left[ \sum_{\langle m \rangle} \langle \lambda_{nm}^0 \lambda_{nm}^0 \rangle S(S+1) \right]^{1/2}, \quad (26)$$

where the numerical constant  $C$  is  $\sqrt{\pi/240} \approx 0.11$ . When the number of nearest neighbors,  $z$ , in the summation  $\langle m \rangle$  is large, we can replace  $\langle \lambda_{nm}^0 \lambda_{nm}^0 \rangle$  by its powder average and obtain

$$D = Ca_0^2 \left[ \left( \frac{4}{5} \right)^{1/2} \frac{\hbar^2 \gamma^2}{a_0^3} \sqrt{zS(S+1)} \right] \quad (27)$$

The result in Eq. (27) should be compared with those of Mori and Kawasaki,<sup>24</sup> and de Gennes<sup>25</sup> for a system of spins coupled by Heisenberg exchange. The former gives a  $C = 0.06$  while the latter gives a  $C = 0.05$ . In making the comparison, we have replaced their exchange constant  $4J$  by  $\sqrt{4/5} \hbar^2 \gamma^2 / a_0^3$ . For a numerical estimate, let  $z = 6$ , as in a cubic lattice, and  $S = \frac{1}{2}$ .

Then

$$D = 0.22 \hbar^2 \gamma^2 / a_0$$

which is in agreement with the results<sup>15</sup> of Lowe and Gade. The diffusion coefficient in Eq. (27) may also be expressed in terms of the local dipolar field,<sup>17</sup>  $H_D$ .

$$H_D^2 = \frac{S(S+1)}{4} \sum_m \langle \lambda_{nm}^0 \lambda_{nm}^0 \rangle,$$

by restricting the summation  $\sum_m$  to the nearest neighbors only. The result is

$$D = \sqrt{\pi/60} a_0^2 H_D \quad (28)$$

### III. SOLUTION FOR RAPID DIFFUSION; $D/t^2 \gg |\Delta A_\alpha|$

In this section and the next, we consider solutions to Eq. (1). Since both mutual spin flip and self-diffusion lead to the same diffusion equation, though the physical origins for the diffusion coefficient  $D$  are different, we shall not make the distinction in the subsequent discussion. Further we shall suppress the subscript  $\alpha = Z, T$  in Eq. (1) whenever no confusion arises.

In the rapid-diffusion limit, Eq. (1) can be evaluated in two ways: (a) by cumulant expansion method<sup>26</sup> and (b) by second-order perturbation theory.<sup>27</sup> Both essentially yield the same results.

#### A. Cumulant expansion method

Let  $V$  be the volume of our system and  $\langle \langle f(\bar{\tau}) \rangle \rangle$  be the spatial average of a function  $f(\bar{\tau})$ , i.e.,

$$\langle \langle f(\bar{\tau}) \rangle \rangle \equiv V^{-1} \int d\bar{\tau} f(\bar{\tau}) \quad (29)$$

$A(\bar{\tau})$  may be rewritten as

$$A(\bar{\tau}) = \langle \langle A(\bar{\tau}) \rangle \rangle + \delta A(\bar{\tau}), \quad (30)$$

where  $\delta A(\bar{\tau})$  is the deviation of  $A(\bar{\tau})$  from its average value. Note that  $\langle \langle \delta A(\bar{\tau}) \rangle \rangle = 0$ . When diffusion dominates Eq. (1), it is convenient to introduce a quantity  $\tilde{M}(\bar{\tau}, t)$  by

$$M(\bar{\tau}, t) \equiv \exp[-\langle \langle A(\bar{\tau}) \rangle \rangle t] \exp D \nabla^2 t \tilde{M}(\bar{\tau}, t) \quad (31)$$

Substituting Eq. (31) into Eq. (1) yields the equation of motion of  $\tilde{M}(\bar{\tau}, t)$

$$\frac{\partial \tilde{M}(\bar{\tau}, t)}{\partial t} = -[\exp(-D \nabla^2 t)] \delta A(\bar{\tau}) \times (\exp D \nabla^2 t) \tilde{M}(\bar{\tau}, t) \quad (32)$$

The equation is formally integrated with the use of a time ordered exponential<sup>26</sup> to

$$\tilde{M}(\bar{\tau}, t) = \left[ \exp_0 \left[ - \int_0^t \delta A(\bar{\tau}, \tau) d\tau \right] \right] \tilde{M}(\bar{\tau}, t=0), \quad (33)$$

where the differential operator  $\delta A(\bar{\tau}, t)$  is defined as

$$\delta A(\bar{\tau}, t) \equiv [\exp(-D \nabla^2 t)] \delta A(\bar{\tau}) (\exp D \nabla^2 t) \quad (34)$$

One should note that  $\exp(D \nabla^2 t)$  is given by the series expansion

$$\exp D \nabla^2 t = 1 + D \nabla^2 t + \frac{1}{2} (D \nabla^2 t)^2 + \dots + \frac{1}{n!} (D \nabla^2 t)^n + \dots \quad (35)$$

and that  $\nabla^2$  acts on everything to its right.

The formal solution of  $M(\bar{r}, t)$  is obtained by substituting Eq. (33) into Eq. (31) and using the fact that  $\tilde{M}(\bar{r}, t=0) = M(\bar{r}, t=0)$ . The observed  $p(t)$ , the average magnetization per unit volume, then becomes

$$p(t) \equiv \langle \langle M(\bar{r}, t) \rangle \rangle = \exp[-\langle \langle A(\bar{r}) \rangle \rangle t] \left\langle \left\langle \exp D \nabla^2 t \left[ \exp_0 - \int_0^t \delta A(\bar{r}, \tau) d\tau \right] M(\bar{r}, t=0) \right\rangle \right\rangle . \quad (36)$$

To proceed further, we assume for simplicity that  $M(\bar{r}, t=0) = p_0$  for all  $\bar{r}$  and introduce a general boundary condition that the volume of our system extends to infinity while every intensive quantity remains finite as  $\bar{r} \rightarrow \infty$ . One of the consequences of the general boundary condition is that

$$\langle \langle \nabla^2 f(\bar{r}) \rangle \rangle = 0 \quad (37)$$

for an intensive quantity  $f(\bar{r})$ . To see that, one first applies Green's first identity to convert the volume integral to a surface one,

$$\langle \langle \nabla^2 f(\bar{r}) \rangle \rangle = V^{-1} \oint \nabla f(\bar{r}) \cdot d\bar{S} ,$$

which is of the order of  $|\nabla f(\bar{r})|(1/|\bar{r}|)$  evaluated on the boundary surface. As  $\bar{r} \rightarrow \infty$ , it vanishes since  $\nabla f(\bar{r})$  remains finite.

Expanding  $\exp(D \nabla^2 t)$  in Eq. (36) in terms of its power series, Eq. (35), and applying Eq. (37), we obtain

$$p(t) = p_0 \exp[-\langle \langle A(\bar{r}) \rangle \rangle t] \left\langle \left\langle \exp_0 \left[ - \int_0^t \delta A(\bar{r}, \tau) d\tau \right] \right\rangle \right\rangle \equiv p_0 \exp[-\langle \langle A(\bar{r}) \rangle \rangle t] \varphi(t) \quad (38)$$

thus defining  $\varphi(t)$ . It is straightforward to expand  $\varphi(t)$  in terms of cumulants,

$$\begin{aligned} \varphi(t) = \exp \left[ - \int_0^t \langle \langle \delta A(\bar{r}, t_1) \rangle \rangle_c dt_1 + \int_0^t \int_0^{t_1} \langle \langle \delta A(\bar{r}, t_1) \delta A(\bar{r}, t_2) \rangle \rangle_c dt_1 dt_2 \right. \\ \left. + \dots + (-1)^n \int_0^t \int_0^{t_1} \dots \int_0^{t_{n-1}} dt_1 \dots dt_n \langle \langle \delta A(\bar{r}, t_1) \dots \delta A(\bar{r}, t_n) \rangle \rangle_c + \dots \right] \quad (39) \end{aligned}$$

where  $\langle \langle \dots \rangle \rangle_c$  denotes the cumulant average. The first term in the exponential vanishes because

$$\langle \langle \delta A(\bar{r}, t) \rangle \rangle_c = \langle \langle \delta A(\bar{r}, t) \rangle \rangle = \langle \langle (\exp D \nabla^2 t) \delta A(\bar{r}) \rangle \rangle = \langle \langle \delta A(\bar{r}) \rangle \rangle = 0 .$$

where Eq. (37) has been used to obtain the third equality. The second cumulant can be written as

$$\begin{aligned} \int_0^t \int_0^{t_1} \langle \langle \delta A(\bar{r}, t_1) \delta A(\bar{r}, t_2) \rangle \rangle_c dt_1 dt_2 \\ = \int_0^t \int_0^{t_1} \langle \langle \delta A(\bar{r}, t_1) \delta A(\bar{r}, t_2) \rangle \rangle dt_1 dt_2 - \int_0^t \int_0^{t_1} \langle \langle \delta A(\bar{r}, t_1) \rangle \rangle \langle \langle \delta A(\bar{r}, t_2) \rangle \rangle dt_1 dt_2 \\ = \int_0^t \int_0^{t_1} \langle \langle \delta A(\bar{r}) [\exp D \nabla^2 (t_1 - t_2)] \delta A(\bar{r}) \rangle \rangle dt_1 dt_2 \\ = \int_0^t (t - \tau) \langle \langle \delta A(\bar{r}) (\exp D \nabla^2 \tau) \delta A(\bar{r}) \rangle \rangle d\tau \\ = \int_0^t (t - \tau) \Psi(\tau) d\tau . \quad (40) \end{aligned}$$

The last equality defines  $\Psi(\tau)$ .

We evaluate  $\Psi(\tau)$  by first introducing the spatial Fourier transform,

$$\delta A(\bar{r}) = (2\pi)^{-3} \int d\bar{q} \delta A(\bar{q}) \exp i\bar{q} \cdot \bar{r} . \quad (41)$$

Then  $\Psi(\tau)$  becomes

$$\begin{aligned} \Psi(\tau) = (2\pi)^{-3} V^{-1} \int d\bar{q} \delta A(\bar{q}) \delta A(-\bar{q}) \\ \times \exp(-Dq^2\tau) . \quad (42) \end{aligned}$$

Using the inverse transform

$$\delta A(\bar{q}) = \int d\bar{r} \delta A(\bar{r}) \exp(-i\bar{q} \cdot \bar{r}) \quad (43)$$

one sees that

$$V^{-1} \delta A(\bar{q}=0) = \langle \langle \delta A(\bar{r}) \rangle \rangle = 0 .$$

Thus the  $\bar{q}=0$  component cannot contribute to  $\Psi(\tau)$ . Moreover, if the average distance between maxima and minima of  $A(\bar{r})$  is  $l$ , then only com-

ponents with  $|\vec{q}| \geq l^{-1}$  will contribute. In other words,  $\Psi(\tau)$  must decay in time faster than  $\exp(-Dl^{-2}\tau)$ .

An alternative expression of  $\Psi(\tau)$  may be given in terms of the spatial correlation  $\langle\langle \delta A(\vec{\tau}) \delta A(\vec{\tau} + \vec{\rho}) \rangle\rangle$ . This is achieved by substituting Eq. (43) into Eq. (42),

$$\Psi(\tau) = (2\pi)^{-3} \int d\vec{q} \int d\vec{\rho} \langle\langle \delta A(\vec{\tau}) \delta A(\vec{\tau} + \vec{\rho}) \rangle\rangle \times \exp(-i\vec{q} \cdot \vec{\rho}) \exp(-Dq^2\tau) \quad (42')$$

The time integral in Eq. (40) may readily be calculated. However the further simplification of

$$\int_0^t (t-\tau) \Psi(\tau) d\tau = t \int_0^\infty \Psi(\tau) d\tau \quad (44)$$

may be achieved whenever the region  $t < l^2/D$  occupies only a small part of the whole domain of  $t$  where  $p(t)$  has significant values. This is always the case for  $A(\vec{\tau}) = -i\omega(\vec{\tau})$  in the rapid-diffusion limit. But for  $A(\vec{\tau}) = T_1(\vec{\tau})^{-1}$ , we need the more restricted condition of  $Dl^{-2} \gg T_1(\vec{\tau})^{-1}$  and  $\Delta(T_1^{-1})$  for all  $\vec{\tau}$ . From Eq. (42)

$$\int_0^\infty \Psi(\tau) d\tau = (2\pi)^{-3} V^{-1} \int d\vec{q} \frac{\delta A(\vec{q}) \delta A(-\vec{q})}{Dq^2}, \quad (45a)$$

and from Eq. (42')

$$\int_0^\infty \Psi(\tau) d\tau = (4\pi D)^{-1} \int d\vec{\rho} \frac{\langle\langle \delta A(\vec{\tau}) \delta A(\vec{\tau} + \vec{\rho}) \rangle\rangle}{|\vec{\rho}|} \quad (45b)$$

Both equations yield a  $\int_0^\infty \Psi(\tau) d\tau$  of the order of  $|\Delta A|(|\Delta A|l^2/D)$ .

Now, consider the higher-order cumulants in Eq. (39). Since  $\exp(D\nabla^2 t)\delta A(\vec{\tau})$  must decay faster than  $\exp(-Dl^{-2}t)$ , the  $n$ th-order cumulant is roughly of the order<sup>26</sup> of

$$t|\Delta A|(|\Delta A|l^2/D)^{n-1};$$

thus in the rapid-diffusion limit of  $D/l^2 \gg |\Delta A|$ , contributions from the  $n > 2$  terms can be neglected. Retaining the expansion to the second order, we obtain the principal results:

$$p_Z(t) = p_0 \exp\{-[\langle\langle T_1(\vec{\tau})^{-1} \rangle\rangle - \Gamma_Z]t\} \quad (46a)$$

and

$$p_T(t) = p_0 \exp[i\langle\langle \omega(\vec{\tau}) \rangle\rangle t - \Gamma_T t], \quad (46b)$$

where  $\Gamma_\alpha$  is defined as

$$\Gamma_\alpha \equiv \frac{1}{4\pi D} \int d\vec{\rho} \frac{\langle\langle \delta \Omega_\alpha(\vec{\tau}) \delta \Omega_\alpha(\vec{\tau} + \vec{\rho}) \rangle\rangle}{|\vec{\rho}|} = (2\pi)^{-3} V^{-1} \int d\vec{q} \frac{\delta \Omega_\alpha(\vec{q}) \delta \Omega_\alpha(-\vec{q})}{Dq^2}, \quad (47)$$

with  $\delta \Omega_Z(\vec{\tau}) = \delta T_1(\vec{\tau})^{-1}$  and  $\delta \Omega_T(\vec{\tau}) = \delta \omega(\vec{\tau})$ .

Since  $\Gamma_\alpha \geq 0$ , Eq. (46a) indicates that  $p_Z(t)$  decays with a longer  $T_1$

$$T_1 = [\langle\langle T_1(\vec{\tau})^{-1} \rangle\rangle - \Gamma_Z]^{-1}$$

than that in Eq. (2) with  $D \rightarrow \infty$ .

The manifestation of motional narrowing<sup>28,29</sup> shows from Eq. (46b) that rapid diffusion leads to a Lorentzian absorption line which sharply peaks at the average frequency  $\langle\langle \omega(\vec{\tau}) \rangle\rangle$  and has a half-width at half height of  $\Gamma_T$ . This contrasts with the motionless ( $D=0$ ) spectrum given by the static distribution  $I(\omega)$  in Eq. (3b).  $I(\omega)$  may take on any shape and its width is roughly given by  $\langle\langle \delta \omega(\vec{\tau}) \delta \omega(\vec{\tau}) \rangle\rangle^{1/2}$ , the square root of its second moment, which is much larger than  $\Gamma_T$ . An important point that should be made is that the motional narrowed linewidth  $\Gamma_T$  is determined by the spatial correlation  $\langle\langle \delta \omega(\vec{\tau}) \delta \omega(\vec{\tau} + \vec{\rho}) \rangle\rangle$ , thus containing spatial information about our system.

## B. Second-order perturbation theory

The normalized eigenfunctions of the operator  $D\nabla^2$  are the plane waves  $V^{-1/2} \exp/i\vec{q} \cdot \vec{\tau}$ . In the rapid-diffusion limit, it is appropriate to expand the spatial part of  $M(\vec{\tau}, t)$  in terms of this complete orthogonal set. To this end, we write

$$M(\vec{\tau}, t) = Y(t) W(\vec{\tau}) \quad (48)$$

and

$$W(\vec{\tau}) = V^{-1/2} \sum_{\vec{q}} C_{\vec{q}} \exp/i\vec{q} \cdot \vec{\tau}, \quad (49)$$

where  $Y(t)$  and  $W(\vec{\tau})$  are only functions of  $t$  and  $\vec{\tau}$ , respectively. Each component of the wave vector  $\vec{q}$  is any integer times  $2\pi V^{-1/3}$ . A discrete  $\vec{q}$  is used instead of the continuous one because most perturbation methods<sup>27</sup> are given in terms of eigenfunctions with discrete eigenvalues; in doing so, our treatment here will conform with standard methods.

Substituting Eqs. (48) and (49) into Eq. (1) leads to

$$\dot{Y}(t) = -\Lambda Y(t) \quad (50)$$

and

$$\sum_{\vec{q}'} \{[\Lambda - Dq^2 - \langle\langle A(\vec{\tau}) \rangle\rangle] \delta_{\vec{q}\vec{q}'} - V^{-1} \delta A(\vec{q} - \vec{q}')\} C_{\vec{q}'} = 0, \quad (51)$$

where  $\delta_{\vec{q}\vec{q}'}$  is the Kronecker symbol and  $\delta A(\vec{q})$  is again given by Eq. (43). The set of equations represented by Eq. (51) will have a nonvanishing solution only if the secular determinant formed from

the coefficients of the unknown  $C_{\vec{q}}$ 's vanishes, i.e.,

$$[[\Lambda - Dq^2 - \langle \langle A(\vec{r}) \rangle \rangle] \delta_{\vec{q}, \vec{q}'} - V^{-1} \delta A(\vec{q} - \vec{q}')] = 0 \quad (52)$$

Since only  $\delta A(\vec{q})$ 's with  $q \geq l^{-1}$  are significant, in the limit of  $Dl^{-2} \gg |\Delta A|$ , the off-diagonal terms  $V^{-1} \delta A(\vec{q} - \vec{q}')$  may be treated as perturbations. Hence according to the standard perturbation theory the eigenfunction  $\chi_{\vec{q}}$  of the operator  $D\nabla^2 - A(\vec{r})$  is, to the first order of  $V^{-1} \delta A(\vec{q} - \vec{q}')$

$$\begin{aligned} \chi_{\vec{q}} &= \exp i \vec{q} \cdot \vec{r} + V^{-1} \sum_{\vec{q}' (\neq \vec{q})} \frac{\delta A(\vec{q}' - \vec{q})}{D(q^2 - q'^2)} \exp i \vec{q}' \cdot \vec{r} \\ &= \exp i \vec{q} \cdot \vec{r} + \sum_{\vec{q}' (\neq \vec{q})} R_{\vec{q}' \vec{q}} \exp i \vec{q}' \cdot \vec{r}, \end{aligned} \quad (53)$$

thus defining  $R_{\vec{q}' \vec{q}}$ ; the eigenvalue  $\Lambda_{\vec{q}}$  is, to the second order

$$\begin{aligned} \Lambda_{\vec{q}} &= \langle \langle A(\vec{r}) \rangle \rangle + Dq^2 \\ &+ V^{-2} \sum_{\vec{q}' (\neq \vec{q})} \frac{\delta A(\vec{q}' - \vec{q}) \delta A(\vec{q} - \vec{q}')}{D(q^2 - q'^2)}. \end{aligned} \quad (54)$$

The solution to Eq. (1) becomes

$$\begin{aligned} M(\vec{r}, t) &= \sum_{\vec{q}} b_{\vec{q}} \chi_{\vec{q}} \exp(-\Lambda_{\vec{q}} t) \\ &= \sum_{\vec{q}} \exp i \vec{q} \cdot \vec{r} \left[ b_{\vec{q}} \exp(-\Lambda_{\vec{q}} t) \right. \\ &\quad \left. + \sum_{\vec{q}' (\neq \vec{q})} R_{\vec{q}' \vec{q}} b_{\vec{q}'} \exp(-\Lambda_{\vec{q}'} t) \right]. \end{aligned} \quad (55)$$

The coefficient  $b_{\vec{q}}$ 's are determined by the initial condition

$$V^{-1/2} C_{\vec{q}} = b_{\vec{q}} + \sum_{\vec{q}' (\neq \vec{q})} R_{\vec{q}' \vec{q}} b_{\vec{q}'} \quad (56)$$

Since  $M(\vec{r}, t)$  can also be expanded as

$$M(\vec{r}, t) = \sum_{\vec{q}} M_{\vec{q}}(t) \exp i \vec{q} \cdot \vec{r}, \quad (57)$$

the initial condition in Eq. (56) becomes

$$M_{\vec{q}}(t=0) = b_{\vec{q}} + \sum_{\vec{q}' (\neq \vec{q})} R_{\vec{q}' \vec{q}} b_{\vec{q}'} \quad (56')$$

Taking the spatial average over Eq. (55), one finds

$$p(t) = b_0 \exp(-\Lambda_0 t) + \sum_{\vec{q} \neq 0} R_{\vec{q} 0} b_{\vec{q}} \exp(-\Lambda_{\vec{q}} t), \quad (58)$$

which reduces to

$$p(t) = p_0 \exp(-\Lambda_0 t), \quad (59)$$

for a uniform  $M(\vec{r}, t=0) = p_0$ . To obtain Eq. (59), we have used the fact that

$$\sum_{\vec{q} \neq 0} R_{\vec{q} 0} \sim |\Delta A| l^2 / D \ll 1.$$

In the limit of  $V \rightarrow \infty$ , the summation  $\sum_{\vec{q}}$  may be replaced by  $V/(2\pi)^3 \int d\vec{q}$ . Then one has

$$\Lambda_0 = \langle \langle A(\vec{r}) \rangle \rangle - (2\pi)^{-3} V^{-1} \int d\vec{q} \frac{\delta A(\vec{q}) \delta A(-\vec{q})}{Dq^2}. \quad (60)$$

The combination of Eqs. (59) and (60) leads to the same results in Eq. (46a) and Eq. (46b) obtained from the cumulant expansion method.

Two comments should be made here. First, without  $\delta A(\vec{q} - \vec{q}')$ ,  $M_{\vec{q}}(t)$  with large  $\vec{q}$  would have decayed to zero rapidly at  $t \sim (Dq^2)^{-1}$ . Now, as indicated by Eq. (55) that

$$\begin{aligned} M_{\vec{q}}(t) &= b_{\vec{q}} \exp(-\Lambda_{\vec{q}} t) \\ &+ \sum_{\vec{q}' (\neq \vec{q})} R_{\vec{q}' \vec{q}} b_{\vec{q}'} \exp(-\Lambda_{\vec{q}'} t), \end{aligned} \quad (61)$$

$\delta A(\vec{q} - \vec{q}')$ 's couple  $M_{\vec{q}}(t)$  to other  $\vec{q}'$  modes, in particular to the  $\vec{q}' = 0$  mode. Thus  $M_{\vec{q}}(t)$  has a slow component which decays with the rate of  $\hat{\Lambda}_0$ , where  $\hat{\Lambda}_0$  stands for the real part of  $\Lambda_0$ . At larger  $t$ , such component dominates others. In other words, at sufficiently large  $t$ ,  $M_{\vec{q} \neq 0}(t)$  will approach zero with the same rate as the slow  $M_{\vec{q}=0}(t)$  mode.

The second remark is that if one chooses to have the initial condition of  $M_{\vec{q}=0}(0) = 0$ ,  $p(t)$  becomes

$$p(t) = \sum_{\vec{q} \neq 0} R_{\vec{q} 0} b_{\vec{q}} [\exp(-\Lambda_{\vec{q}} t) - \exp(-\Lambda_0 t)]. \quad (62)$$

Instead of decaying monotonically in time,  $p(t)$  first grows from  $p(t=0) = 0$  as time increases and then decays back to zero with a rate constant of  $\hat{\Lambda}_0$ .

### C. Evaluations of $\Gamma_{\alpha}$

The calculation of  $\Gamma_{\alpha}$  is simplest when there are only few  $\vec{q}$  components in  $\delta\Omega(\vec{r})$ . For example, a sinusoidal  $\delta\Omega(\vec{r})$

$$\delta\Omega(\vec{r}) = \Delta\Omega \cos \vec{k} \cdot \vec{r},$$

yields

$$\Gamma_{\alpha} = 4\Delta\Omega / Dk^2. \quad (63)$$

In other cases, the decomposition of  $\delta\Omega(\vec{r})$  into its Fourier components is not always that straightforward; very often,  $\delta\Omega(\vec{r})$  is not known *a priori*. Nevertheless, we are able to calculate  $\Gamma_{\alpha}$  explicitly for two cases which are quite general in nature and may have some practical applications.

In the first case, we assume a globular distribution of  $\delta\Omega(\vec{r})$  as depicted in Fig. 1. Our system consists of spheres with radius roughly  $l_g$  and  $\Omega(\vec{r}) = \Omega_1$  embedded in the background where  $\Omega(\vec{r}) = \Omega_2$ . The average separation  $R$  between spheres is assumed to



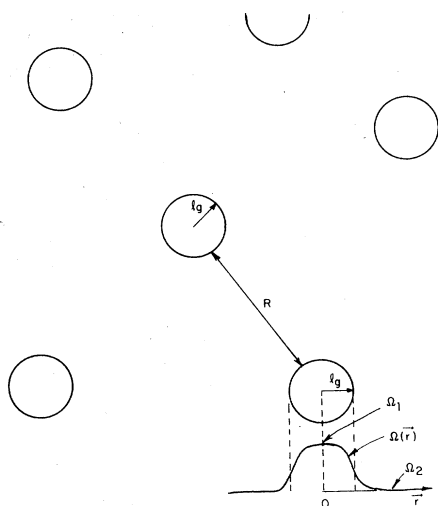


FIG. 1. Spatial distribution of  $\Omega(\vec{r})$  in the globular model.

be so large that  $R^2/D$  is much longer than any NMR experimental time scale. In other words, the spheres are isolated and cannot communicate with one another through spin diffusion within a NMR time scale. Thus the center of any particular sphere may be conveniently chosen to be the origin of our coordinate system, as shown in Fig. 1.

The variation of  $\Omega(\vec{r})$  as a function of  $\vec{r}$  is chosen to be a Gaussian

$$\Omega(\vec{r}) = (\Omega_1 - \Omega_2) \exp(-|\vec{r}|^2/l_g^2) + \Omega_2 \quad (64)$$

At  $|\vec{r}| \gg l_g$ ,  $\Omega(\vec{r}) = \Omega_2$  and at  $|\vec{r}| \leq l_g$ ,  $\Omega(\vec{r}) \approx \Omega_1$ . The calculations of  $\Gamma_\alpha$  are rather simple. In the limit of  $N\nu/V \ll 1$ , one finds

$$\Gamma_\alpha = C_1 (\Omega_1 - \Omega_2)^2 \left( \frac{l_g^2}{D} \right) \left( \frac{N\nu}{V} \right), \quad (65)$$

with the numerical constant  $C_1$  given by

$$C_1 = 3 \int_0^\infty d\rho \int_0^\infty dr \rho r^2 \exp[-(2r^2 + \rho^2 + 2\vec{r} \cdot \vec{\rho})]$$

$N$  is the number of spheres in the sample and  $\nu \equiv \frac{4}{3}\pi l_g^3$  is roughly the volume of each sphere.

The second case we consider is that of a complete randomness in the spatial distribution of  $\Omega(\vec{r})$  in which  $\Omega(\vec{r})$  can take on only two values, i.e.,  $\Omega(\vec{r}) = \Omega_1$  or  $\Omega_2$ . We shall first consider the situation where the number of sites with  $\Omega_1$  is equal to that of  $\Omega_2$  and then extend to a general ratio later.

In the former, one may use the fact, that  $\delta\Omega(\vec{r})$  can only take on two values of opposite sign but of equal magnitude, to obtain the spatial correlation in

Eq. (47) of the following form

$$\begin{aligned} & \langle \langle \delta\Omega(\vec{r}) \delta\Omega(\vec{r} + \vec{\rho}) \rangle \rangle \\ &= \langle \langle \delta\Omega(\vec{r}) \delta\Omega(\vec{r}) \rangle \rangle \sum_{n=0}^{\infty} P_n(\vec{\rho}) (-1)^n \quad (66) \end{aligned}$$

$P_n(\vec{\rho})$  is the probability that  $\delta\Omega(\vec{r})$  has changed sign  $n$  times when we go from site  $\vec{r}$  to site  $\vec{r} + \vec{\rho}$ . Since the spatial distribution is completely random, we can assume the Poisson distribution for  $P_n(\vec{\rho})$

$$P_n(\vec{\rho}) = \frac{1}{n!} \left( \frac{|\vec{\rho}|}{l_c} \right)^n \exp\left(-\frac{|\vec{\rho}|}{l_c}\right), \quad (67)$$

where the correlation length  $l_c$  represents the mean distance between sites that have opposite sign in  $\delta\Omega(\vec{r})$ . Now Eq. (66) becomes

$$\begin{aligned} \langle \langle \delta\Omega(\vec{r}) \delta\Omega(\vec{r} + \vec{\rho}) \rangle \rangle &= \frac{1}{4} (\Omega_1 - \Omega_2)^2 \\ &\times \exp(-2|\vec{\rho}|/l_c) \quad (68) \end{aligned}$$

Substituting this into Eq. (47), gives

$$\Gamma_\alpha = \frac{1}{16} (\Omega_1 - \Omega_2)^2 (l_c^2/D) \quad (69)$$

For the general situation, in which the fraction of sites with  $\Omega_1$  is  $a$  [the fraction of sites with  $\Omega_2$  is thus  $(1-a)$ ],  $\delta\Omega(\vec{r})$  again can only take on two values of opposite sign which may differ in magnitude. Because of the inequality in the number of sites with  $\Omega_1$  and  $\Omega_2$ , it is convenient to introduce two probability functions:  $P'(\vec{\rho})$  and  $P''(\vec{\rho})$ , where the former represents the probability that given  $\Omega(\vec{r}) = \Omega_1$ ,  $\Omega(\vec{r} + \vec{\rho})$  equals  $\Omega_1$  while the latter represents the probability that given  $\Omega(\vec{r}) = \Omega_2$ ,  $\Omega(\vec{r} + \vec{\rho})$  equals  $\Omega_2$ . The spatial correlation function is then evaluated to be

$$\begin{aligned} & \langle \langle \delta\Omega(\vec{r}) \delta\Omega(\vec{r} + \vec{\rho}) \rangle \rangle \\ &= (\Omega_1 - \Omega_2)^2 a \{ (1-a)^2 P'(\vec{\rho}) \\ &\quad - a(1-a)[1 - P'(\vec{\rho})] \} \\ &\quad + (\Omega_1 - \Omega_2)^2 (1-a) \{ a^2 P''(\vec{\rho}) \\ &\quad - a(1-a)[1 - P''(\vec{\rho})] \} \quad (70) \end{aligned}$$

Since  $P'(\vec{\rho}) = a$  and  $P''(\vec{\rho}) = (1-a)$  as  $\vec{\rho} \rightarrow \infty$ , and  $P'(0) = P''(0) = 1$ , one may write

$$P'(\vec{\rho}) \equiv a + (1-a)\tilde{P}'(\vec{\rho}) \quad (71)$$

and

$$P''(\vec{\rho}) \equiv (1-a) + a\tilde{P}''(\vec{\rho}) \quad (72)$$

The normalized probabilities  $\tilde{P}'(\vec{\rho})$  and  $\tilde{P}''(\vec{\rho})$  have the obvious properties of

$$\tilde{P}'(\vec{\rho} \rightarrow \infty) = \tilde{P}''(\vec{\rho} \rightarrow \infty) = 0$$

and

$$\bar{P}'(0) = \bar{P}''(0) = 1$$

Substituting Eqs. (71) and (72) into Eq. (70) yields

$$\begin{aligned} \langle \langle \delta\Omega(\vec{r})\delta\Omega(\vec{r} + \vec{\rho}) \rangle \rangle &= a(1-a)(\Omega_1 - \Omega_2)^2 \\ &\times [(1-a)\bar{P}'(\vec{\rho}) + a\bar{P}''(\vec{\rho})] \end{aligned} \quad (73)$$

Similar to Eq. (68), we may associate  $\bar{P}'(\vec{\rho})$  and  $\bar{P}''(\vec{\rho})$  with two correlation lengths,  $l'_c$  and  $l''_c$ , by

$$\bar{P}'(\vec{\rho}) = \exp(-2|\vec{\rho}|/l'_c)$$

and

$$\bar{P}''(\vec{\rho}) = \exp(-2|\vec{\rho}|/l''_c)$$

The correlation length  $l'_c$  ( $l''_c$ ) represents the mean distance at which, if one starts from a site with  $\Omega_1$  ( $\Omega_2$ ), one will find a site with  $\Omega_2$  ( $\Omega_1$ ). It is a simple matter to show that

$$\Gamma_\alpha = a(1-a)(\Omega_1 - \Omega_2)^2 [(1-a)l'_c{}^2 + al''_c{}^2]/4D \quad (74)$$

When  $a = \frac{1}{2}$  (hence  $l'_c = l''_c$ ), Eq. (74) reduces to Eq. (69).

In more general cases, one may always introduce several correlation lengths and  $\delta\Omega(\vec{r})$ , and obtains a general expression

$$\langle \langle \delta\Omega(\vec{r})\delta\Omega(\vec{r} + \vec{\rho}) \rangle \rangle = \sum_n (\delta\Omega_n)^2 \exp\left(\frac{-2|\vec{\rho}|}{l_{cn}}\right) \quad (75)$$

Substituting this into the first equality in Eq. (47) leads to

$$\Gamma_\alpha = \sum_n (\delta\Omega_n)^2 \frac{l_{cn}^2}{4D} \quad (76)$$

which bears a close resemblance to the second equality in Eq. (47). However there is a basic difference between them; the latter requires the complete knowledge of the spatial dependence of  $A(\vec{r})$  to determine  $\Gamma_\alpha$  whereas only the statistical distribution in  $A(\vec{r})$  around any particular site is required for the former.

#### IV. SOLUTIONS FOR SLOW DIFFUSION:

$$Dl^{-2} \ll |A(\vec{r})|, |\Delta A|$$

It is convenient to introduce  $M(\vec{r}, s)$ , the Laplace transform of  $M(\vec{r}, t)$

$$M(\vec{r}, s) = \int_0^\infty e^{-st} M(\vec{r}, t) dt \quad (77)$$

and to rewrite Eq. (1) as

$$\begin{aligned} M(\vec{r}, s) &= [s + A(\vec{r})]^{-1} + [s + A(\vec{r})]^{-1} D \nabla^2 M(\vec{r}, s) \\ &\equiv G(\vec{r}, s) + G(\vec{r}, s) D \nabla^2 M(\vec{r}, s) \end{aligned} \quad (78)$$

$M(\vec{r}, s)$  reduces to  $G(\vec{r}, s)$  in the limit of  $D \rightarrow 0$ .

We have assumed that  $M(\vec{r}, t=0)$  is the same for all  $\vec{r}$  and, without loss of generality, equals to unity.

In the slow-diffusion limit,  $D \nabla^2$  can be treated as a perturbation; its effects on  $M(\vec{r}, s)$  may be expressed linearly in  $M(\vec{r}, s)$ . Namely, using the linear approximation that

$$\nabla M(\vec{r}, s) \simeq -G(\vec{r}, s) [\nabla A(\vec{r})] M(\vec{r}, s) \quad (79)$$

we obtain

$$\begin{aligned} D \nabla^2 M(\vec{r}, s) &= D \{ 2[\nabla A(\vec{r})]^2 G(\vec{r}, s)^2 \\ &\quad - [\nabla^2 A(\vec{r})] G(\vec{r}, s) \} M(\vec{r}, s) \\ &\equiv Dh(\vec{r}, s) M(\vec{r}, s) \end{aligned} \quad (80)$$

thus defining  $h(\vec{r}, s)$ . Such linear approximations hold for all  $s$  when  $A(\vec{r})$  is real but are limited to  $s$  with large real part,  $\hat{s}$ , when  $A(\vec{r})$  is imaginary. We shall return to this shortly. A special feature of Eq. (80) is that  $h(\vec{r}, t)$ , the inverse Laplace transform of  $h(\vec{r}, s)$ , becomes a memory function in the equation of motion of  $M(\vec{r}, t)$ . To see that, one substitutes Eq. (80) into Eq. (78) and rearranges terms to obtain

$$M(\vec{r}, s) = [s + A(\vec{r}) - Dh(\vec{r}, s)]^{-1} \quad (81)$$

The inverse transform is

$$\begin{aligned} \dot{M}(\vec{r}, t) &= -A(\vec{r}) M(\vec{r}, t) \\ &\quad + D \int_0^t h(\vec{r}, t - \tau) M(\vec{r}, \tau) d\tau \end{aligned} \quad (82)$$

To proceed further, we must treat the cases of  $A(\vec{r}) = -i\omega(\vec{r})$  and  $A(\vec{r}) = T_1(\vec{r})^{-1}$  separately. As have been mentioned earlier, when  $A(\vec{r})$  is imaginary, the linear approximation is appropriate only for  $s$  with large  $\hat{s}$ . The reason is that for  $A(\vec{r}) = -i\omega(\vec{r})$ ,  $G(\vec{r}, s)$  has poles only on the imaginary axis in the complex  $s$  plane. Spin diffusion leads to the dephasing of the transverse magnetization; the decay of  $M_T(\vec{r}, t)$  at large  $t$  is reflected by the shifts of these poles onto the left half  $s$  plane. An important point is that  $M_T(\vec{r}, t)$  with  $t \rightarrow \infty$  is characterized by  $M_T(\vec{r}, s)$  with  $s \rightarrow 0$ . Thus  $G(\vec{r}, s)$  is inadequate to describe  $M_T(\vec{r}, s)$  in the limit of  $s \rightarrow 0$ . However, when  $\hat{s}$  is much larger than the real parts of the poles of  $M_T(\vec{r}, s)$ , the difference between  $G(\vec{r}, s)$  and  $M_T(\vec{r}, s)$  becomes insignificant. On the other hand, when  $A(\vec{r}) = T_1(\vec{r})^{-1}$ , the poles of  $G(\vec{r}, s)$  are located on the real axis. Spin diffusion may lead to slight shifts of these poles along the real axis as well as introduce small imaginary parts. But since  $T_1(\vec{r})^{-1}$  dominates the time evolution of  $M_Z(\vec{r}, t)$  for all  $t$ ,  $M_Z(\vec{r}, s)$  is adequately described by  $G(\vec{r}, s)$  for all  $s$ .

A. Imaginary  $A(\vec{r})$ :  $A(\vec{r}) = -i\omega(\vec{r})$

We shall first examine the short-time behavior of  $M_T(\vec{r}, t)$  where the linear approximation is adequate. Substituting Eq. (80) into Eq. (82) and using the fact that at small  $t$

$$\int_0^t e^{-i\omega(\vec{r})\tau} M_T(\vec{r}, \tau) d\tau \approx te^{-i\omega(\vec{r})t} M_T(\vec{r}, t)$$

and

$$\int_0^t (t-\tau) e^{-i\omega(\vec{r})\tau} M_T(\vec{r}, \tau) d\tau \approx \frac{t^2}{2} e^{-i\omega(\vec{r})t} M_T(\vec{r}, t)$$

leads to

$$\begin{aligned} \dot{M}_T(\vec{r}, t) = & i\omega(\vec{r})M_T(\vec{r}, t) \\ & + D \{ [i\nabla^2\omega(\vec{r})]t - [\nabla\omega(\vec{r})]^2 t^2 \} \\ & \times M_T(\vec{r}, t), \end{aligned} \quad (83)$$

which is formally integrated to give

$$\begin{aligned} M_T(\vec{r}, t) = \exp \left\{ i\omega(\vec{r})t + i\frac{D}{2} [\nabla^2\omega(\vec{r})]t^2 \right. \\ \left. - \frac{D}{3} [\nabla\omega(\vec{r})]^2 t^3 \right\}. \end{aligned} \quad (84)$$

Thus the first-order corrections to the zeroth order  $\omega(\vec{r})t$  are of the order of  $(tDl^{-2})(\Delta\omega t)$  and  $(tDl^{-2})(\Delta\omega t)^2$ . To extend Eq. (84) to longer  $t$ , one may have to include higher-order corrections which involve the operator  $(D\nabla^2)^n$ , where  $n \geq 2$ . However, an important point is that since  $M_T(\vec{r}, t)$  decays at least with a time constant  $\zeta(\vec{r})^{-1}$ , where

$$\zeta(\vec{r}) = \{ D [\nabla\omega(\vec{r})]^2 / 3 \}^{1/3}, \quad (85)$$

if the higher-order corrections are significant only when  $t \gg \zeta(\vec{r})^{-1}$ , as would be the case when  $\omega(\vec{r})$  is a weakly varying function of  $\vec{r}$  such that

$$l|\nabla\omega(\vec{r})| \gg l^n |\nabla^n\omega(\vec{r})| \text{ for } n \geq 2, \quad (86)$$

then  $M_T(\vec{r}, t)$  in Eq. (84) holds essentially for all  $t$ . Moreover, with the exception that  $\vec{r}$  is at the local extremum of  $\omega(\vec{r})$ , Eq. (84) reduces to

$$M_T(\vec{r}, t) = \exp[i\omega(\vec{r})t - \zeta^3(\vec{r})t^3]. \quad (84')$$

In particular, when  $\omega(\vec{r})$  takes on the form

$$\omega(\vec{r}) = \omega_0 + \vec{K} \cdot \vec{r},$$

where  $\omega_0$  and  $\vec{K}$  are independent of  $\vec{r}$ , Eq. (84') is exact. Explicitly, one has

$$M_T(\vec{r}, t) = \exp[i\omega(\vec{r})t - D|\vec{K}|^2 t^3 / 3]. \quad (84'')$$

Equation (84'') has been derived by others using different methods,<sup>6-9</sup> and has been used to describe the effect of spin diffusion on the evolution of the transverse magnetization when the external field varies linearly across the sample. Our Eq. (84') may be considered as the generalization to the case in which  $\vec{K}$  is a function of  $\vec{r}$ .

Physically, Eq. (84') and the approximations it represents can be understood as follows. When  $D = 0$ ,  $M_T(\vec{r}, t)$ 's at different sites differ only in their phases but their amplitudes remain constant, i.e.,

$$|M_T(\vec{r}, t)| = |M_T(\vec{r}, t=0)| = 1,$$

since there is no communication between spins. A nonvanishing  $D$  leads to the dephasing of  $M_T(\vec{r}, t)$ . Consequently  $M_T(\vec{r}, t)$  decays with a rate of  $\zeta(\vec{r})$ . Since  $\zeta(\vec{r})$  may be site dependent, i.e., a function of  $\vec{r}$ ,  $M_T(\vec{r}, t)$ 's at different sites now differ not only in their phases but also in their amplitudes. The differences in amplitudes cause further actions from spin diffusion which tends to average out such differences. Mathematically, the further actions from spin diffusion are represented by the higher-order correction terms mentioned above. Thus the higher-order corrections are important only when  $\zeta(\vec{r})$  varies rapidly as a function of  $\vec{r}$  such that the differences in the amplitudes of  $M_T(\vec{r}, t)$ 's become significant at times  $t \leq \zeta^{-1}(\vec{r})$ . If the inequality in Eq. (86) holds, the effects of the higher corrections would not be felt until  $t \gg \zeta(\vec{r})^{-1}$  at which  $M_T(\vec{r}, t)$  essentially decays to zero. Hence in practical terms, Eq. (84') is valid for all  $t$ .

It is illustrative to derive Eq. (84') from another point of view. The formal solution for  $M(\vec{r}, s)$  can be obtained by iterating Eq. (78)

$$M(\vec{r}, s) = G(\vec{r}, s) [1 + D\nabla^2 G(\vec{r}, s) + D^2\nabla^2 G(\vec{r}, s)\nabla^2 G(\vec{r}, s) + \cdots + D^n\nabla^2 G(\vec{r}, s) \cdots \nabla^2 G(\vec{r}, s) + \cdots]. \quad (87)$$

Using Eq. (86) and neglecting all  $\nabla^n\omega(\vec{r})$  but  $\nabla\omega(\vec{r})$  leads to

$$M_T(\vec{r}, s) = \sum_{n=0}^{\infty} D^n [i\nabla\omega(\vec{r})]^{2n} \frac{3n!}{3^n n!} G^{3n+1}(\vec{r}, s), \quad (88)$$

whose inverse transform is simply

$$M_T(\vec{r}, t) = e^{i\omega(\vec{r})t} \sum_{n=0}^{\infty} \frac{\{D[i\nabla\omega(\vec{r})]^2 t^3 / 3\}^n}{n!} \equiv \exp\{i\omega(\vec{r})t - D[\nabla\omega(\vec{r})]^2 t^3 / 3\}.$$

B. Real  $A(\bar{r})$ :  $A(\bar{r}) = T_1(\bar{r})^{-1}$

In this case, the linear approximation is valid for all  $s$ . Substituting Eq. (80) into Eq. (78) yields

$$M_Z(\bar{r}, s) = \frac{G(\bar{r}, s)^{-2}}{G(\bar{r}, s)^{-3} + G(\bar{r}, s)^{-1}\beta_2^2 - \beta_1^3} \quad (89)$$

where

$$\beta_1^3 = 2D \left[ \nabla \frac{1}{T_1(\bar{r})} \right]^2$$

and

$$\beta_2^2 = D \nabla^2 \frac{1}{T_1(\bar{r})}$$

The denominator is a polynomial cubic in  $s$ ; the poles of  $M_Z(\bar{r}, s)$  are given by the roots of the cubic equation. With the inequality similar to Eq. (86),  $\beta_1^3$  is expected to be much larger than  $\beta_2^2$  except at the local extremum of  $T_1(\bar{r})^{-1}$ ; thus one of the roots is real while the other two are complex conjugate. For  $\beta_1^3 \gg \beta_2^2 \sim 0$ , one finds that the poles are located at

$$\begin{aligned} s_1 &= -T_1(\bar{r})^{-1} + \beta_1, \\ s_2 &= -T_1(\bar{r})^{-1} - \beta_1(1 - i\sqrt{3})/2, \\ s_3 &= -T_1(\bar{r})^{-1} - \beta_1(1 + i\sqrt{3})/2, \end{aligned} \quad (90)$$

and that

$$\begin{aligned} M_Z(\bar{r}, t) &= \frac{1}{3} \exp\{-[T_1(\bar{r})^{-1} - \beta_1]t\} \\ &\quad + \frac{2}{3} \exp\{-[T_1(\bar{r})^{-1} + \beta_1/2]t\} \\ &\quad \times \cos(\sqrt{3}\beta_1 t/2). \end{aligned} \quad (91a)$$

Equation (91a) is remarkably different from Eq. (84'), though they agree to the lowest-order expansion in  $D$ . If we had used the short-time approximation that leads to Eq. (83), we would have obtained

$$M_Z(\bar{r}, t) = \exp[-t/T_1(\bar{r}) + \beta_1^3 t^3/6], \quad (91b)$$

which is appropriate only for  $t \ll [\beta_1^3 T_1(\bar{r})]^{-1/2}$ . Indeed, as  $t \rightarrow \infty$ , Eq. (91b) gives the nonphysical result of  $M_Z(\bar{r}, t) \rightarrow \infty$ . The reason is that, as discussed in the derivation of Eqs. (84') and (84''), Eq. (91b) is appropriate only if one can expand  $T_1(\bar{r})^{-1}$  as

$$T_1(\bar{r})^{-1} = T_1(\bar{r}_0)^{-1} + \bar{K}(\bar{r}_0) \cdot (\bar{r} - \bar{r}_0),$$

where  $\bar{r}_0$  is some reference point and  $\bar{K}(\bar{r}_0)$  is weakly dependent on  $\bar{r}_0$ . It is exact when  $K(\bar{r}_0)$  is a constant. This implies that we may write Eq. (1) as

$$\begin{aligned} \dot{M}_Z(\bar{r}, t) &= D \nabla^2 M_Z(\bar{r}, t) \\ &\quad - [T_1(\bar{r}_0)^{-1} + \bar{K}(\bar{r}_0) \cdot (\bar{r} - \bar{r}_0)] M_Z(\bar{r}, t). \end{aligned}$$

But

$$[T_1(\bar{r}_0)^{-1} + \bar{K}(\bar{r}_0) \cdot (\bar{r} - \bar{r}_0)]$$

can become negative as  $\bar{r} \rightarrow \infty$  or  $\bar{r} \rightarrow -\infty$  depending on the direction of  $\bar{K}(\bar{r}_0)$ ; thus we have artificially created source points in our system which lead to the growth of  $M_Z(\bar{r}, t)$  as  $t \rightarrow \infty$ .

A closer examination indicates that one cannot represent  $T_1(\bar{r})^{-1}$  in Eq. (1) by any finite expansion in  $\bar{r}$ ,

$$T_1(\bar{r})^{-1} = \sum_{m=0}^{m=n} a_m(\bar{r})^m. \quad (92)$$

If  $n$  is odd, we always have  $T_1(\bar{r})^{-1} < 0$  as  $\bar{r} \rightarrow \infty$  or  $\bar{r} \rightarrow -\infty$ . For even  $n$ , we have  $T_1(\bar{r})^{-1} \rightarrow \pm \infty$  depending on the sign of  $a_n$ . While  $a_n > 0$  does not lead to the source point contradiction, it implies that at sufficiently large  $\bar{r}$ ,  $M_Z(\bar{r}, t)$  always decays infinitely fast. Furthermore the sign of  $a_n$  depends on the location of the reference point  $\bar{r}_0$ ; therefore the expansion in Eq. (92) is not unique, nor is the solution.

The reason that  $\nabla[1/T_1(\bar{r})]$  suffices for  $M_Z(\bar{r}, t)$ , as indicated by Eq. (91a), may be understood as follows. The iteration of Eq. (81) shows that

$$M_Z(\bar{r}, s) = G(\bar{r}, s) \sum_{n=0}^{\infty} [D \nabla^2 G(\bar{r}, s)]^n. \quad (93)$$

Now  $\nabla^2$  acts only on  $G(\bar{r}, s)$  to its immediate right. Neglecting terms with  $\nabla^2[1/T_1(\bar{r})]$  and performing the inverse Laplace transform yields Eq. (91a). Thus the infinite series in Eq. (87) is summed differently for the case of  $A(\bar{r}) = 1/T_1(\bar{r})$  and  $A(\bar{r}) = -i\omega(\bar{r})$ . In the latter,  $\nabla^2$  acts on everything to its right. Namely, the  $n$ th term in the expansion in Eq. (87) may be written as

$$\begin{aligned} D^n \nabla^2 G(\bar{r}, s) \cdots \nabla^2 G(\bar{r}, s) \\ = D^n \{ 2[\nabla A(\bar{r})]^2 G(\bar{r}, s)^3 \}^n \\ + D^n \left[ [\nabla A(\bar{r})]^{2n} \frac{3n!}{3^n n!} G(\bar{r}, s)^{3n} \right] + D^n [\cdots], \end{aligned} \quad (94)$$

where the ellipsis represents terms with  $\nabla^n A(\bar{r})$ , where  $n \geq 2$ . The first two terms on the right-hand side involve only  $\nabla A(\bar{r})$ . Retaining only the first term and then summing the series, we obtain Eq. (91a). On the other hand, summing only the second term, one gets Eq. (84') instead. Therefore the nature of  $A(\bar{r})$  dictates which terms in Eq. (94) should be retained for the summation. In either case, when

$$|\nabla A(\bar{r})| \gg |^n \nabla^n A(\bar{r})|,$$

for  $n \geq 2$ ,  $\nabla A(\bar{r})$  suffices for  $M(\bar{r}, t)$ .

For the sake of completeness, we should discuss the situation in which  $\bar{r}$  is at local extremum of

$T_1(\bar{\tau})^{-1}$  where  $\beta_1 = 0$ . Here, the denominator in Eq. (89) reduces to a polynomial quartic in  $s$ ; the poles of  $M_Z(\bar{\tau}, s)$  are obtained by solving the quartic equation. Their locations on the complex  $s$  plane depend on the sign of  $\beta_2^2$  which can be either positive or negative depending on whether  $\bar{\tau}$  is at a local minimum or maximum on  $T_1(\bar{\tau})^{-1}$ . For  $\beta_2^2 > 0$

$$s_1 = -T_1(\bar{\tau})^{-1} - i|\beta_2|, \quad s_2 = -T_1(\bar{\tau})^{-1} + i|\beta_2|,$$

and

$$M_Z(\bar{\tau}, t) = \exp[-t/T_1(\bar{\tau})] \cos|\beta_2|t;$$

for  $\beta_2^2 < 0$

$$s_1 = -T_1(\bar{\tau})^{-1} - |\beta_2|, \quad s_2 = -T_1(\bar{\tau})^{-1} + |\beta_2|,$$

and

$$M_Z(\bar{\tau}, t) = \exp[-t/T_1(\bar{\tau})] \cosh|\beta_2|t.$$

### C. Evaluations of the decay rate of $p(t)$

We first consider the case of  $A(\bar{\tau}) = -i\omega(\bar{\tau})$ . The effect of spin diffusion on the transverse magnetization can be best seen by following the decay of the amplitude of a spin echo<sup>6</sup> as a function of the delay time  $t$  between the initial preparation pulse and the peak of the spin echo. This decay is described by

$$p_{\text{se}}(t) = \langle \langle \exp\{-[\zeta(\bar{\tau})t]^3\} \rangle \rangle, \quad (95)$$

where the subscript se stands for spin echo. Since the decay of each spin is characterized by  $\zeta(\bar{\tau})$ , the decay rate  $\bar{\zeta}$  of  $p_{\text{se}}(t)$  may be defined as the spatial average

$$(\bar{\zeta})^3 = \langle \langle \zeta^3(\bar{\tau}) \rangle \rangle = -\left. \frac{\partial p_{\text{se}}(t)}{\partial t^3} \right|_{t=0}. \quad (96)$$

The second equality indicates how such a quantity may be determined experimentally.

$(\bar{\zeta})^3$  involves  $\langle \langle [\nabla\omega(\bar{\tau})]^2 \rangle \rangle$  which can be evaluated for simple models. For instance, let us again consider the globular model described in Sec. III C in which aggregates (need not be spherical in shape) of spins with  $\omega(\bar{\tau}) = \omega_1$  are surrounded by spins with  $\omega(\bar{\tau}) = \omega_2$ . For simplicity, we shall assume a constant  $|\nabla\omega(\bar{\tau})|$  at the interface of width  $w$  and area  $b$ . Since  $|\nabla\omega(\bar{\tau})|$  is nonvanishing only at the interface, we easily find that

$$(\bar{\zeta})^3 = \frac{D}{3} |\nabla\omega|^2 \frac{Nwb}{V}, \quad (97)$$

where  $N$  is again the number of aggregates in the sample. Now suppose that the aggregates are spherical in shape with a radius  $l_g \gg w$ . Then  $b = 4\pi l_g^2$  and  $(\bar{\zeta})^3$  becomes

$$\begin{aligned} (\bar{\zeta})^3 &= D |\nabla\omega|^2 (Nv/V)(w/l_g) \\ &= D (\omega_1 - \omega_2)^2 (Nv/V)(wl_g)^{-1}, \end{aligned} \quad (98)$$

where  $v = \frac{4}{3}\pi l_g^3$ . The approximation of  $|\nabla\omega| = |\omega_1 - \omega_2|/w$  at the interface has been used to obtain the second equality. As for the case for  $\Gamma_\alpha$  in Sec. III C,  $\bar{\zeta}$  depends on the geometric parameters of the system. Indeed, from Eq. (98), one sees that  $\bar{\zeta}$  is inversely proportional to  $(wl_g)^{1/3}$ .

Another interesting model is the spatially stochastic distribution of two well-separated resonances  $\omega_1$  and  $\omega_2$  whose relative abundance are  $a$  and  $(1-a)$ , respectively (cf. Sec. III C). Here the decay of each species of spins can be followed. For the spins with  $\omega_1$  and  $\omega_2$ , the decay rate constants, given by Eq. (85) are, respectively.

$$\zeta_1 = \left[ \frac{Dz}{6} (1-a) \left( \frac{\omega_1 - \omega_2}{a_0} \right)^2 \right]^{1/3} \quad (99)$$

and

$$\zeta_2 = \left[ \frac{Dz}{6} a \left( \frac{\omega_1 - \omega_2}{a_0} \right)^2 \right]^{1/3}. \quad (100)$$

$a_0$  and  $z$  are, respectively, the lattice constant and the number of nearest neighbors that each site has as defined in Sec. II. The factor of  $(1-a)$  in Eq. (99) represents the probability that a given site has  $\omega(\bar{\tau}) = \omega_2$ , whereas the factor of  $a$  in Eq. (100) represents the probability that a given site has  $\omega(\bar{\tau}) = \omega_1$ .

Two remarks are in order. First, in contrast with the motional narrowing in the limit of large  $D$ , each resonance line is now broadened by spin diffusion in the limit of small  $D$ . The half-widths at half height are roughly  $\zeta_1$  and  $\zeta_2$ . This agrees with the motional broadening due to slow exchange between two frequencies originally discussed by Anderson.<sup>28</sup> The second remark is that for  $a \neq \frac{1}{2}$ , the two resonance lines are broadened differently: the larger component of the two absorptions is narrower than the smaller one.

It is more difficult to characterize the effects of spin diffusion on the decay of  $p(t)$  for  $A(\bar{\tau}) = T_1(\bar{\tau})^{-1}$  in the sense that the definition of  $\bar{\zeta}$  can be quite arbitrary, as may be seen from Eq. (91a). We shall conveniently choose the definition,<sup>30</sup>

$$(\bar{\zeta})^{-1} = \int_0^\infty \frac{p(t)}{p(t=0)} dt \equiv \langle \langle M(r, s=0) \rangle \rangle, \quad (101)$$

because a larger (smaller) area under  $p(t)/p(t=0)$  reflects a slower (faster) decay of  $p(t)$ . With this definition, one obtains from Eq. (89) that

$$(\bar{\zeta})^{-1} = \langle \langle T_1(\bar{\tau}) [1 + T_1(\bar{\tau})^3 \beta_1^3] \rangle \rangle, \quad (102)$$

where the  $\beta_2$  term has been neglected and the fact that  $T_1(r)^{-1} \gg \beta_1$  has been used. The difference in the decay time  $\Delta\tau$  between that of Eq. (102) and that

with  $D = 0$  is

$$\begin{aligned}\Delta\tau &= (\bar{\zeta})^{-1} - \langle \langle T_1(\bar{\tau}) \rangle \rangle \\ &= 2D \langle \langle T_1(\bar{\tau})^4 \{ \nabla [1/T_1(\bar{\tau})] \}^2 \rangle \rangle \geq 0\end{aligned}$$

## V. DISCUSSION

Spin diffusion leads to communication among spins at various sites in a solid. We have shown that such communication may provide useful information about the spatial inhomogeneity in the resonance frequencies and relaxation times. The rate of the spin-flip communication is directly proportional to the local dipolar field.

Our approach to the problem of rapid diffusion ( $Dl^{-2} \gg |\Delta A|$ ) is similar to that in the stochastic theory of resonance absorption introduced by Anderson<sup>28</sup> and Kubo.<sup>29</sup> The equation of motion in Eq. (1) permits us to determine the time dependence of the time correlation  $\Psi(t)$  explicitly, thereby reducing  $\Psi(t)$  to a spatial correlation function. On the other hand, our formulation of the slow diffusion [ $Dl^{-2} \ll |A(\bar{\tau})|, |\Delta A|$ ] closely resembles the field-theoretic many-body theory.<sup>31</sup> Indeed,  $M(\bar{\tau}, s)$  and  $G(\bar{\tau}, s)$  in Eq. (78) are, respectively, the analogs of the many-body and single-particle Green's functions. The different ways in the summation of the infinite series in Eq. (87) [cf. Eq. (94)] for the case of  $A(\bar{\tau}) = -i\omega(\bar{\tau})$  and  $A(\bar{\tau}) = T_1(\bar{\tau})^{-1}$  represent the different renormalization procedures by which  $G(\bar{\tau}, s)$  is "dressed" to include the many-body effect.

In disordered solids like glassy polymers, it is quite common to observe multicomponent decay in the magnetization. The usual interpretation is that the different relaxation times correspond to different spatial phases in the sample. Magnetization-recovery ex-

periments<sup>3-5</sup> indicated that these phases may communicate with each other via spin diffusion. However such experiments are confined to systems where the differences in the relaxation times are large. Their interpretations also vary according to the model used.

Recent advances<sup>32</sup> in solid state NMR provide alternative techniques by which one may alter the spin-flip diffusion coefficient by modulating the dipolar interactions. Thus the rate of the communication between spins may be artificially controlled. Magic angle spinning<sup>33</sup> can suppress spin-flip diffusion when the spinning speed is comparable or larger than the local dipolar field. Since  $T_1(\bar{\tau})^{-1}$  [or  $T_{1\rho}(\bar{\tau})^{-1}$  in the rotating frame] and the spin-flip diffusion coefficient  $D$  are determined by different frequency components of the spectral density of the dipolar interactions (see Sec. II), magic angle spinning which suppresses the spin-flip diffusion may leave  $T_1(\bar{\tau})^{-1}$  [or  $T_{1\rho}(\bar{\tau})^{-1}$ ] unaltered. Thus spin diffusion can be monitored by studying the NMR relaxations as a function of the spinning speed.

Multiple pulse techniques also suppress dipolar interactions. They provide high resolution absorption spectra in which the dipolar broadening is eliminated. The effectiveness of the suppression of the dipolar interactions depends on the cycle time used. Thus multiple pulse techniques may provide alternative ways by which the effects of spin diffusion can be studied.

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