

Variational calculation of NMR relaxation of diffusing ions by impurity centers

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(Received 3 August 1981)

The relaxation rate of a diffusing spin influenced by an impurity center is treated. We present both a qualitative scaling argument which can predict the dependence of the rate on various parameters and a variational principle which can be used to obtain a quantitative result accurate to within about 12% for a simple trial function. The methods should be useful for the study of NMR in fast ion conductors in situations, such as anisotropic diffusion in a low-dimensional system or impurity-influenced diffusion rate, where exact solutions of a continuum diffusion equation with a sink are not obtainable. For example, we treat (i) the standard three-dimensional case with a r^{-6} interaction and compare the simple variational calculation with the known exact result, and (ii) a quasi-one-dimensional system which has not previously been solved.

I. INTRODUCTION

The motion of rapidly diffusing light ions is central to such topics of current interest as superionic conductors, metal hydrides, and muons in solids. NMR [or muon spin rotation (μ SR)] has proven to be a most effective probe of this motion.¹ Although much information can be gained by motional linewidth narrowing of the interaction with other nuclear spins and spin-lattice relaxation caused by coupling with host nuclei and electric field gradients (efg), for spin $> \frac{1}{2}$, relaxation due to impurity centers can often be an even more effective probe.²⁻⁴ Basically this is because, if the impurities are stationary, only single-particle motion is involved whereas relative motion of two particles or a particle and a vacancy are required to describe nuclear dipole-dipole or efg interactions. Further, in the slow hopping region where relaxation is controlled by the time it takes a spin to diffuse to the center, the observed relaxation rate is nearly independent of interaction strength and thus a rather direct measure of single-particle diffusion. Relaxation by impurities can also be used as a "tagging" method² to determine which species is diffusing in complex solid electrolytes.

The most commonly studied type of impurity has been the paramagnetic ion. If one is fortunate enough to have a dominantly nearest-neighbor-only interaction, as is the case^{2,3} in $\text{PbF}_2\text{:Mn}$, resulting from a transferred hyperfine coupling which greatly exceeds the classical dipole-dipole value, the problem can be solved analytically^{3,5} in terms of discrete hopping and the correct lattice geometry accounted for.³ However, the long-range dipolar interaction is not amenable to such relatively simple treatment. In this case one generally resorts to a continuum approximation although a recent numerical calculation has been done for a discrete lattice.^{4,6} The magneti-

zation at point \vec{r} influenced by an impurity at the origin is described in the continuum model by

$$\frac{\partial M_\alpha}{\partial t} = \vec{\nabla} \cdot [D(\vec{r}) \vec{\nabla} M_\alpha] - \eta_\alpha(\vec{r})(M_\alpha - M_\alpha^0) \quad (1)$$

Here M_α is the component of \vec{M} (understood to be in the rotating frame if α is a component transverse to the applied field) whose equilibrium value is M_α^0 , $\eta_\alpha(\vec{r})$ is the relaxation rate assumed to exist⁵ if the spin is held fixed at \vec{r} , and $D(\vec{r})$ is a diffusion coefficient which we allow to be anisotropic and dependent on \vec{r} in general.

For the case of isotropic, homogeneous diffusion $D(\vec{r}) = D$ and average dipole interaction $\eta_\alpha(\vec{r}) = \eta_0 r^{-6}$, Eq. (1) can be solved in the steady state in terms of Bessel functions and the relaxation rate for the spatially averaged magnetization determined.^{5,7,8} Nonetheless, at least two problems provide motivation for approximate, simple solutions to the more general case. The first concerns quasi-one-dimensional (1D) systems where D is highly anisotropic. The Li ion conductor LiAlSiO_4 (β -eucryptite) is an excellent example, and recent NMR studies have been made on iron-doped samples of the material.⁹ The second is in regard to work on PbF_2 doped with alkali ions¹⁰ which shows that non-paramagnetic centers can be important. Here one does not expect a simple r^{-6} dependence of $\eta_\alpha(\vec{r})$ and the diffusion coefficient may be a function of r .

The purpose of the present work is therefore to provide an approximate treatment of the continuum model of Eq. (1) which can be used in important cases where an exact solution is not possible. We first present a scaling argument which gives the form of the bulk relaxation rate and then derive a variational principle which is applied to the quasi-1D system and also worked out for the 3D case. The latter is done in order to provide a means of comparing the

result obtained with a simple trial function to an exact calculation. Attention is confined to slow hopping (rate limited by time it takes to diffuse to region of impurity) since it is known⁵ that in the fast hopping regime the interaction may adequately be approximated by nearest neighbor [see argument under Eq. (10)] and thus the discrete hopping techniques employed.

II. QUALITATIVE SCALING ARGUMENT

We show here how the familiar⁸ slow-hopping result $T^{-1} \propto N(C/D)^{1/4}D$ may be derived by a simple scaling argument. Here T is the relaxation time, a dipolar $\eta_\alpha(r) = Cr^{-6}$ is assumed, $D(\vec{r}) = D$ is isotropic and homogeneous and N is the number of impurities per unit volume. The value of such an argument is that it can, as done here, readily be applied to other situations.

In the slow hopping case $T \approx T_0$, where T_0 is the average time required for a diffusing ion to first encounter an impurity, it is being assumed that relaxation effectively takes place instantly once the impurity is encountered. We imagine that the sample of total volume V is divided into $V/\Delta V$ regions each of whose volumes ΔV represents the volume over which an impurity is active. This is, if the ion is not in a region ΔV which contains an impurity, it experiences no relaxation, but it is relaxed once it diffuses within an impurity-containing region. For a nearest-neighbor interaction obviously $\Delta V = a_0^3$, where a_0 is the nearest-neighbor interaction distance. The relation between ΔV and $\eta(r)$ and D will be discussed shortly. For the moment we take ΔV as given and define $\tilde{\tau}$ as the time a diffusing particle spends in ΔV . For isotropic diffusion and ΔV , the effective hopping time is $\tilde{\tau} \sim (\Delta V)^{2/3}/D$. Since there are $t/\tilde{\tau}$, different ΔV 's visited in time t , and the probability that a given ΔV contains an impurity is $N\Delta V$, we have

$$N_{\text{imp}} = N\Delta V t / \tilde{\tau} \quad (2)$$

where N_{imp} is the average number of impurities encountered in time t . The slow-hopping relaxation time is that time for which $N_{\text{imp}} = 1$, so the rate is

$$T^{-1} = N\Delta V / \tilde{\tau} \sim Nr_0 D \quad (3)$$

where the latter expression holds for an isotropic diffusion and ΔV with $\Delta V = r_0^3$.

The size of ΔV is determined by equating

$$\tilde{\tau} = 1/\eta(r_0) \quad (4)$$

where $\eta(r_0)^{-1}$ is the time it takes to relax at the boundary. [We are now assuming an isotropic $\eta(\vec{r}) = \eta(r)$.] The sense of Eq. (4) is that if $\eta(r_0)\tilde{\tau} < 1$ the particle does not spend sufficient time in the region to be relaxed. If, for example,

$\eta(r) = Cr^{-n}$ and $\tilde{\tau} = r_0^2/D$ for isotropic diffusion, Eq. (4) gives $r_0 = (C/D)^{1/(n-2)}$ and from (3)

$$T^{-1} \sim ND(C/D)^{1/(n-2)} \quad (5)$$

so that the $(C/D)^{1/4}$ dependence is recovered for $n = 6$.

The usefulness of the argument is better illustrated for quasi 1D where the solution is not already known. Here the particle diffusion is highly anisotropic with $D_{\parallel} \gg D_{\perp}$ where D_{\parallel} and D_{\perp} are components of D parallel and perpendicular to the 1D channel, respectively. (We assume that spin diffusion, which may be nearly 3D even in the channel structures is negligible at the relatively high temperatures of interest.) The region ΔV is still spherical as long as $\eta(\vec{r})$ depends only on r . Some care must be executed in the calculation of $\tilde{\tau}(r_0)$ to use in Eq. (4). The time *initially* to hop out of the region is of the order of r_0^2/D_{\parallel} for $D_{\parallel} \gg D_{\perp}$ since it is sufficient to move just along the channel. However, if the motion is restricted to 1D, the particle makes repeated returns to the region, so that the time the particle actually spends within r_0 , which is the proper definition of $\tilde{\tau}$, tends to infinity. More precisely, for a 1D random walk of duration t , a particle spends an amount of time of the order of $(r_0^2 t / D_{\parallel})^{1/2}$ within a distance r_0 of the origin. Hence, it is *not* correct to take $\tilde{\tau} = r_0^2/D_{\parallel}$. As shown in Appendix A, the proper choice is

$$\tilde{\tau} \approx r_0^2 / (D_{\parallel} D_{\perp})^{1/2} \quad (6)$$

for the time spent within a distance r_0 of the origin.

Use of Eqs. (6) and (4) thereby gives

$$r_0 = (C/\sqrt{D_{\parallel} D_{\perp}})^{1/(n-2)} \quad (7)$$

We determine the number of impurities encountered in time t as follows. The regions ΔV form chains as shown in Fig. 1. A particle stays on a given chain for an average time $\tau_{\perp} \approx r_0^2/D_{\perp}$ and hops between regions on a chain at a rate $\tau_{\parallel}^{-1} = D_{\parallel}/r_0^2$.

For $t/\tau_{\perp} \gg 1$, the number of different chains encountered in time t is $N_{\text{chains}} = t/\tau_{\perp}$. During the time τ_{\perp} spent on a given chain, $\tau_{\perp}/\tau_{\parallel}$ "hops" (jumps between regions) are made and a distance $r_0(\tau_{\perp}/\tau_{\parallel})^{1/2}$ is covered, in which $(\tau_{\perp}/\tau_{\parallel})^{1/2}$ different regions of length r_0 are visited, i.e., a 1D random walk. The number of impurities encountered is then the number of chains encountered \times number of regions per chain, \times number of impurities per region, and thus

$$N_{\text{imp}} = \left[\frac{t}{\tau_{\perp}} \right] \left[\frac{\tau_{\perp}}{\tau_{\parallel}} \right]^{1/2} N\Delta V = t(\tau_{\perp}\tau_{\parallel})^{-1/2} N\Delta V \quad (8)$$

so, analogous to Eq. (3), we have

$$T^{-1} = N\Delta V / (\tau_{\perp}\tau_{\parallel})^{1/2} \sim Nr_0(D_{\perp}D_{\parallel})^{1/2} \quad (9)$$

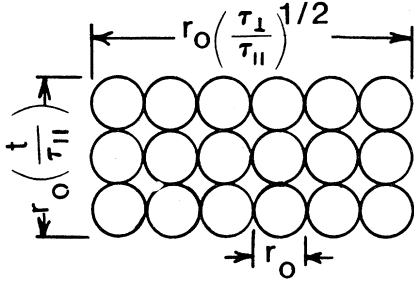


FIG. 1. Quasi-1D lattice divided into chains of spheres of radius r_0 . In time $t \gg \tau_{\perp}$, $(\tau_{\perp}/\tau_{\parallel})^{1/2}$ spheres are visited on each chain and t/τ_{\perp} different chains are visited.

Use of (7) then gives

$$T^{-1} \sim NC^{1/(n-2)}(D_{\perp}D_{\parallel})^{(1/2)(n-3)/(n-2)}, \quad (10)$$

a relation which is confirmed by the variational calculation presented in Sec. III.

The above considerations make sense only if the distance $r_0 \sim (\Delta V)^{1/3}$ is larger than the distance of closest approach, which is just the near-neighbor distance a_0 for simple hopping. If the calculated r_0 in Eq. (4) or (7) is less than a_0 , the particle does not stay in the neighborhood of an impurity long enough to be relaxed, and the interaction is effective only at nearest-neighbor distance. Then, as mentioned in the Introduction, one can regard the interaction as nearest neighbor. Also, the argument is valid only if r_0 is much less than the distance between impurities, i.e., $N\Delta V \ll 1$. Otherwise the range is sufficiently long that it is not necessary for the particle to diffuse to the center.

III. VARIATIONAL METHOD

It is convenient to consider the Laplace transform of Eq. (1)

$$\bar{\nabla} \cdot (D \bar{\nabla} \psi) - \eta \psi - s \psi + \Delta M(0) = 0, \quad (11)$$

where

$$\psi = \int_0^{\infty} dt e^{-st} [M_{\alpha}(\bar{r}, t) - M_{\alpha}^0],$$

$$\Delta M(0) = M_{\alpha}(\bar{r}, t=0) - M_{\alpha}^0,$$

and all quantities in Eq. (11) except the laplace variable s may be functions of position \bar{r} . The complete equation has

$$\eta = \sum_j \eta(\bar{r} - \bar{r}_j),$$

where the sum is over all impurity sites and the boundary condition is that there be no diffusion

across the surface of the sample. The usual technique^{5,7} for low-impurity concentration is to assume that each impurity acts independently and to solve Eq. (11) for $\eta = \eta(\bar{r})$, that is a single impurity at the origin, with the boundary condition of no diffusion across an outer surface S_0 . The volume enclosed by S_0 is $V_0 = N^{-1}$, the average volume per impurity [note the difference between V_0 and ΔV (Sec. II), the volume over which an impurity is *effective*]. No diffusion is also assumed to take place across an inner surface S_i , which for an isotropic $\eta(r)$ and normal particle diffusion is just a sphere of radius a_0 , the distance (nearest-neighbor) of closest approach.

The standard variational approach¹¹ is to allow ψ to change to $\psi + \delta\psi$ in the interior bounded by S_i and S_0 but to satisfy the proper boundary conditions, which in this case means $\hat{n} \cdot D \bar{\nabla} \delta\psi = 0$ on S_i and S_0 where \hat{n} is a unit vector normal to the surface. By multiplying Eq. (11) by $\delta\psi$, integrating over the volume, making use of the divergence theorem and the identities $\psi \delta\psi = \frac{1}{2} \delta(\psi^2)$, $\bar{\nabla} \delta\psi \cdot D \bar{\nabla} \psi = \frac{1}{2} \delta(\bar{\nabla} \psi \cdot D \bar{\nabla} \psi)$ for a small change $\delta\psi$ one obtains

$$\delta I = 0, \quad (12)$$

where the integral I is

$$I = \int_{V_0} d^3r [2\psi \Delta M(0) - (s + \eta)\psi^2 - \bar{\nabla} \psi \cdot D \bar{\nabla} \psi], \quad (13)$$

and thus is stationary with respect to small perturbations from the correct solution. One can further show that

$$I = \int_{V_0} d^3r \psi_0 \Delta M(0) \equiv I_0, \quad (14)$$

if ψ_0 is the exact solution and that $I < I_0$ for any other function ψ which satisfies the boundary conditions. Thus the variational calculation proceeds by choosing a trial function which satisfies the boundary conditions and whose parameters are chosen to maximize I . We perform the calculation below first for an isotropic $D(\bar{r}) = D$ and $\eta(r) = Cr^{-6}$ where the approximate solution may be compared with the known result and then for the highly anisotropic quasi-1D system where an exact solution is not known.

A. Isotropic diffusion

For isotropic diffusion and relaxation $\eta(r)$ it is evident that the outer surface S_0 must be a sphere of radius R and that $4\pi R^3/3 = 1/N$. The inner surface S_i is a sphere of radius a_0 and $\psi(\bar{r})$ is of course a function of r only. For slow hopping the impurity is effective over a distance $r_0 > a_0$ as discussed in Sec. II, so we may imagine that $\psi = 0$ (i.e., the spins are completely relaxed) for $r \leq r_0$. The trial function is therefore chosen to be zero for $r \leq r_0$ where r_0 is

now a parameter to be determined by the maximization of I . As long as the result gives $r_0 \geq a_0$ the boundary condition on S_i , $(\partial\psi/\partial r)_{a_0} = 0$, is obviously satisfied. Other treatments of the problem⁸ have also employed an approximate solution which is zero within a critical distance from the impurity. To a first approximation, the relaxation term $\eta(r)$ can be ignored for $r > r_0$ so that Eq. (11) reduces to the radial wave equation whose solution has $\partial\psi/\partial r \propto 1/r^2$ for small r . That is, the current crossing a sphere of radius r is independent of r .

We therefore pick as a simple trial function

$$\psi = \begin{cases} \frac{A}{R^2} (r - r_0) \left(\frac{R^2}{r} - r_0 \right), & r \geq r_0 \\ 0, & r \leq r_0 \end{cases} \quad (15)$$

($r_0 \geq a_0$) which satisfies the boundary conditions $\partial\psi/\partial r = 0$ at a_0 and R and which has

$$\frac{\partial\psi}{\partial r} = \frac{Ar_0}{R^2} \left(\frac{R^2}{r^2} - 1 \right)$$

proportional to $1/r^2$ for $r \ll R$.

The parameters A and r_0 are determined by using (15) in (13) and maximizing the resulting integral I . For $R \gg r_0$ we have

$$I \approx \frac{8}{3} \pi \Delta M(0) A R^3 - \frac{4}{3} \pi s A^2 R^3 - \frac{8 \pi A^2 C r_0^{3-n}}{(n-1)(n-2)(n-3)} - 4 \pi A^2 D r_0, \quad (16)$$

where we have taken $\eta(r) = cr^{-n}$ with $n > 3$. Maximizing I with respect to A gives

$$\bar{\psi} = \frac{\Delta M(0)}{s + \Gamma}, \quad (17)$$

where $\bar{\psi} = A$ is the volume average and

$$\Gamma = R^{-3} \left[3r_0 D + \frac{6Cr_0^{3-n}}{(n-1)(n-2)(n-3)} \right], \quad (18)$$

The simple form of Eq. (17) shows that the average magnetization decays as a single exponential with rate Γ . Maximizing I with respect to r_0 gives

$$r_0 = \left[\frac{2(C/D)}{(n-1)(n-2)} \right]^{1/(n-2)}, \quad (19)$$

whereby (18) may be rewritten as

$$\Gamma = 4\pi N D r_0 \left[1 + \frac{1}{n-3} \right], \quad (20)$$

where we have used $4\pi R^3/3 = N^{-1}$ with N the number of impurities per cm^3 .

For $n = 6$, we have $r_0 = 0.56(C/D)^{1/4}$ and $\Gamma = 9.4ND(C/D)^{1/4}$. The exact result^{5,7,8,12} is $\Gamma = 8.4ND(C/D)^{1/4}$, so we are able to come within about 12% with the simple trial function. If the problem is replaced by one in which $\eta(r) = 0$ for $r > r_0$ and $\eta(r) \rightarrow \infty$ for $r < r_0$, i.e., complete relaxation within r_0 and no relaxation beyond r_0 , it is found^{8,12} that $r_0 = 0.68(C/D)^{1/4}$. Note that our method overestimates Γ . This is as expected since Eq. (17) shows that I is proportional to $1/\Gamma$, and I is a maximum for the correct solution.

For future reference (Sec. III B) it is useful to note that as long as $r_0 \ll R$, the trial function $\psi = A[1 - (r_0/r)](r > r_0)$ gives the same results as obtained with Eq. (15), and this is simply the solution to Laplace's equation which is zero at r_0 .

B. Quasi 1D

The problem is assumed to have axial symmetry, so we write Eq. (11) in cylindrical coordinates as

$$D_{\parallel} \left[\frac{\partial^2 \psi}{\partial z^2} + \frac{\lambda}{\rho} \frac{\partial}{\partial \rho} \left(\rho \frac{\partial \psi}{\partial \rho} \right) \right] - (\eta + s)\psi + \Delta M(0) = 0, \quad (21)$$

where $\lambda = D_{\perp}/D_{\parallel} \ll 1$ and $\rho^2 = x^2 + y^2$. We choose the geometry of the outer surface S_0 by demanding that the current \vec{J} just inside S_0 should be radial inward. The rationale for this is that if \vec{J} is not so directed, the particle will prefer to move to another impurity, which leads to an obvious contradiction to the definition of S_0 as the surface within which the impurity at the origin is influential. The current is given by

$$\vec{J} = D_{\parallel} \left[\hat{z} \frac{\partial \psi}{\partial z} + \lambda \hat{\rho} \frac{\partial \psi}{\partial \rho} \right], \quad (22)$$

where \hat{z} and $\hat{\rho}$ are unit vectors. A radial current means $\vec{J} \times \hat{r} = 0$, where $\hat{r} = (z\hat{z} + \rho\hat{\rho})/r$. The condition for this from (22) is

$$\lambda z \frac{\partial \psi}{\partial \rho} = \rho \frac{\partial \psi}{\partial z},$$

which is satisfied if

$$\psi = \psi(z^2 + \rho^2/\lambda). \quad (23)$$

Thus we choose S_0 as an ellipsoid of revolution (prolate spheroid) described by

$$z^2 + \rho^2/\lambda = R^2 \quad (24)$$

as sketched in Fig. 2. The semimajor axis R is chosen to make the volume equal the volume per impurity,

$$\frac{4\pi}{3}\lambda R^3 = N^{-1} . \quad (25)$$

The highly prolate shape of S_0 makes good sense physically. Since motion in the $z(\parallel)$ direction is much easier than in the $\rho(\perp)$ direction, an ion can be attracted to an impurity much further away in the \parallel than in the \perp direction. Indeed the relation from (24) $z_{\max}^2/\rho_{\max}^2 = \lambda^{-1} = D_{\parallel}/D_{\perp}$ says that the times to diffuse a parallel distance z_{\max} and a perpendicular distance ρ_{\max} should be comparable, where $z_{\max} = R$ and $\rho_{\max} = \lambda^{1/2}R$ are the parallel and perpendicular dimensions, respectively, over which the impurity is influential.

It is convenient to make a change of variables $\rho' = \rho/\lambda^{1/2}$ whereby Eq. (21) becomes

$$D_{\parallel}\nabla^2\psi - [\eta(z^2 + \lambda\rho'^2) + s]\psi + \Delta M(0) = 0 , \quad (26)$$

and the outer and inner surfaces are $r' = R$ and $z^2 + \lambda\rho'^2 = a_0^2$, respectively, where $r'^2 = z^2 + \rho'^2$ and the Laplacian $\nabla^2\psi$ is with respect to z and ρ' . The problem thus is transformed to one with isotropic diffusion and a spherical outer boundary but with oblate spheroidal inner boundary and surfaces of constant η , as indicated in Fig. 3. The fact that the same transformation both changes $\vec{\nabla} \cdot D \vec{\nabla}$ to the normal Laplacian and makes S_0 spherical confirms the geometry chosen for S_0 .

We now construct a trial function which satisfies $\partial\psi/\partial n = 0$ at S_0 and, by analogy with the treatment of the isotropic problem, has $\psi = 0$ between S_1 and some intermediate surface S' . Further analogy suggests that ψ satisfy Laplace's equation in the region between S' and S_0 . This is facilitated by the use of oblate spheroidal coordinates¹³ ξ and u related to ρ and z by

$$\rho^2 = a^2(1 + \xi^2)(1 - u^2) , \quad (27a)$$

$$z = a\xi u , \quad (27b)$$

where $|u| \leq 1$, $0 \leq \xi < \infty$. (Axial symmetry is assumed so that the azimuthal coordinate is not need-

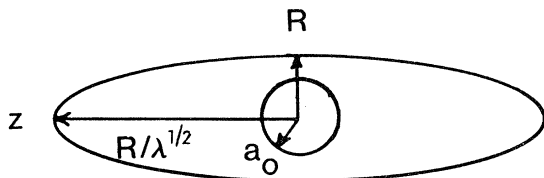


FIG. 2. Inner and outer surfaces on which $\partial\psi/\partial n = 0$ for quasi-1D diffusion. $\lambda = D_{\perp}/D_{\parallel}$.

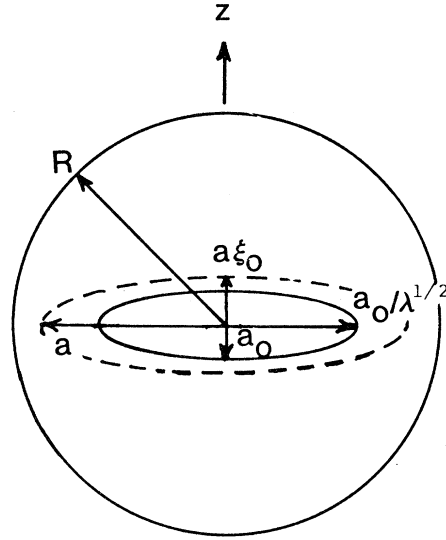


FIG. 3. Surfaces of Fig. 2 in transformed coordinates. Dashed curve is surface $\xi = \xi_0$ within which trial function has $\psi = 0$.

ed.) Surfaces of constant ξ are recognized as oblate spheroids which, for $\xi \ll 1$, resemble disks of radius a and thickness $2a\xi$. The trial function which satisfies $\psi = 0$ on the surface $\xi = \xi_0$ and is a solution to Laplace's equation is¹³

$$\psi = \begin{cases} 0, & \xi < \xi_0 \\ A (\tan^{-1}\xi - \tan^{-1}\xi_0) / (\frac{1}{2}\pi - \tan^{-1}\xi_0), & \xi \geq \xi_0 . \end{cases} \quad (28)$$

The value $\xi_0 = \lambda^{1/2}$ is seen, by comparing Eqs. (26) and (27) for $\lambda \ll 1$, to make the surface $\xi = \xi_0$ be one of constant relaxation rate. This is the logical choice, but for the moment we choose to keep ξ_0 , as well as the characteristic length a , a parameter to be used in maximizing the variational integral I . The trial function (28) makes sense only if $\xi \approx R/a \gg 1$ at the outer boundary so that ψ goes to the constant value A . We also must have (see Fig. 3) $\lambda^{1/2}a > a_0$ and $a\xi_0 > a_0$. This imposes a relation between the anisotropy ratio D_{\perp}/D_{\parallel} and the impurity concentration to be discussed later. We also must have (see Fig. 3) $\lambda^{1/2}a > a_0$ and $a\xi_0 > a_0$.

The maximization of I is carried out in Appendix B. The relaxation rate for $\xi_0 \ll 1$, $R/a \gg 1$ is found to be

$$\Gamma = 7.2NC^{1/4}(D_{\perp}D_{\parallel})^{3/8} , \quad (29)$$

and the characteristic distance is

$$a = 0.67(C/D_{\parallel})^{1/4}(D_{\parallel}/D_{\perp})^{5/8} , \quad (30)$$

for $\eta(r) = Cr^{-6}$. The integral I is independent of ξ_0

as long as $\xi_0 \ll 1$, so that no optimum value of ξ_0 is found in this approximation.

For $\xi_0 \ll 1$ the perpendicular dimension (in the untransformed coordinates) of the surface on which $\psi = 0$ is $\rho_0 \approx \lambda^{1/2} a = 0.67 (C/\sqrt{D_{\perp} D_{\parallel}})^{1/4}$. This and the form (29) are consistent with the scaling argument presented in Sec. II.

The condition $R/a \gg 1$ which is necessary for a linear concentration dependence may be expressed as

$$(D_{\perp}/D_{\parallel}) \gg \rho^{8/7} (\eta_0 \tau_0)^{6/7}, \quad (31)$$

where $\rho = Na_0^3$ is of the order of the number of impurities per lattice site, $\eta_0 = C/a_0^3$ is the relaxation rate at the nearest-neighbor distance a_0 and $\tau_0 = a_0^2/D_{\parallel}$ is the 1D hopping time. For a highly 1D system, where $D_{\perp}/D_{\parallel} \sim 10^{-3}$, the above condition is rather stringent and departures from a linear concentration dependence may be expected for concentrations as small as 0.5 at. %

Comparison with experiments on the quasi-1D system LiAlSiO_4 (β -eucryptite) is discussed elsewhere.¹⁴

IV. CONCLUSIONS

We have presented a physical scaling argument and variational principle for calculating relaxation of diffusing spins by impurity centers. These can be useful in situations where the diffusion may be anisotropic and/or position dependent and the interaction strength is not the simple r^{-6} dipolar form, so analytic solution of the diffusion equation with a sink is not possible. Low-dimensional systems and the case¹⁰ where the impurity alters the diffusion rate are examples where the methods may be applied. Often one is

mainly interested in the form of the result, such as dependence of the relaxation rate on the weak inter-channel diffusion D_{\perp} for a quasi-1D system, and it is here where the present techniques are particularly helpful.

As an example, we derived an expression for the relaxation rate in a quasi-1D material which, based on the success of a similar trial function for 3D, should be accurate to within about 12%.

ACKNOWLEDGMENTS

I am grateful to D. Brinkmann, M. Engelsberg, and I. J. Lowe for helpful discussions. The latter two kindly informed me of their studies of Ref. 10. This work is supported by the U.S. Department of Energy (DOE) under Contract No. DE-AC04-76-DP00789.

APPENDIX A

We derive here Eq. (6), the expression for the average time $\bar{\tau}$, a diffusing particle spends within a distance r_0 of the origin. It is given by

$$\bar{\tau} = \int_0^{\infty} d\tau P(r \leq r_0, \tau), \quad (A1)$$

where $P(r < r_0, \tau)$ is the probability the particle is within r_0 at time τ and is expressed as

$$P(r \leq r_0, \tau) = \int_0^{r_0} d^3r p(\vec{r}, \tau), \quad (A2)$$

with $p(\vec{r}, \tau)$ the probability of being at position \vec{r} at time τ . For long times we have the standard result for anisotropic diffusion.

$$p(\vec{r}, \tau) = (2\sqrt{\pi})^{-3} (D_{\perp}\tau)^{-1} (D_{\parallel}\tau)^{-1/2} \exp(-\rho^2/4D_{\perp}\tau) \exp(-z^2/4D_{\parallel}\tau),$$

with $\rho^2 = x^2 + y^2$. This is normalized so that $\int d^3r p(\vec{r}, \tau) = 1$. Since

$$\int_0^{\infty} u^{-3/2} e^{-u^{-1}} du = 2 \int_0^{\infty} e^{-v^2} dv,$$

the time integration in (A1) is readily performed with the result

$$\bar{\tau} = \frac{1}{2D_{\perp}D_{\parallel}^{1/2}} \int_0^{r_0} r^2 dr \int_0^{\pi/2} \frac{\sin\theta d\theta}{[(r^2 \sin^2\theta/4D_{\perp}) + (r^2 \cos^2\theta/4D_{\parallel})]^{1/2}}. \quad (A3)$$

It is easy to see that the result for $D_{\perp} \ll D_{\parallel}$ then becomes

$$\bar{\tau} = \frac{1}{4} \pi r_0^2 / \sqrt{D_{\perp} D_{\parallel}}. \quad (A4)$$

APPENDIX B

We maximize the integral I using the trial function of Eq. (28) for the quasi-1D system. In terms of the

oblate spheroidal coordinates (27) the volume element is¹³

$$d^3r = 2\pi a^3 (\xi^2 + u^2) d\xi du \quad (B1)$$

for axial symmetry and the required gradient is

$$|\nabla\psi|^2 = \frac{\xi^2 + 1}{\xi^2 + u^2} \left(\frac{\partial\psi}{\partial\xi} \right)^2 a^{-2}. \quad (B2)$$

The separate parts of I are then given by $I = I_1 + I_2 + I_3 + I_4$ with

$$I_1 = 2\Delta M(0) \int d^3r \psi = \frac{2A \Delta M(0) \int_{V_0} d^3r (\tan^{-1}\xi - \tan^{-1}\xi_0)}{\frac{1}{2}\pi - \tan^{-1}\xi_0} \approx 2AV_0\Delta M(0) \quad , \quad (\text{B3})$$

$$I_2 = -s \int_{V_0} d^3r |\psi|^2 \approx -sA^2V_0 \quad , \quad (\text{B4})$$

$$I_3 = -D_{\parallel} \int_{V_0} d^3r |\nabla\psi|^2 \approx -8A^2a \quad (\text{B5})$$

($V_0 = \frac{4}{3}R^3$), if $\xi_0 \ll 1$, $R/a \ll 1$. The ‘‘sink’’ integral

$$I_4 = -C \int_{V_0} d^3r |\psi|^2 (\lambda\rho^2 = z^2)^{-3}$$

is written as

$$I_4 = -\frac{16}{\pi} \frac{A^2C}{\lambda^3 a^3} \int_{\xi_0}^{R/a} \frac{d\xi (\tan^{-1}\xi - \tan^{-1}\xi_0)^2}{(1 + \xi^2)^3} F(\xi) \quad , \quad (\text{B6})$$

where

$$F(\xi) = \int_0^1 du (\xi^2 + u^2) [1 + K^2 u^2]^{-3} = \xi^2 \left(\frac{3}{8} \frac{\tan^{-1}K}{K} + \frac{1}{2(1+K^2)} + \frac{1-K^2}{8(1+K^2)^2} \right) + \frac{1}{16K^2} \left(\frac{\tan^{-1}K}{K} - \frac{1}{1+K^2} \right) \quad , \quad (\text{B7})$$

with $K^2 = [\xi^2(1-\lambda) - \lambda]/\lambda(1+\xi^2)$.

Since the integrand of (B6) is largest for $\xi \sim 1$ (as opposed to $\xi \ll 1$) and $\lambda = D_{\perp}/D_{\parallel} \ll 1$, we can use the $K \gg 1$ approximation for $F(\xi)$ and thereby reduce (B6) to

$$I_4 \approx -\frac{16}{\pi} \frac{A^2C}{\lambda^3 a^3} \int_{\xi_0}^{R/a} d\xi \frac{(\tan^{-1}\xi - \tan^{-1}\xi_0)^2}{(1 + \xi^2)^3} \frac{3\pi}{16} \lambda^{1/2} (1 + \xi^2)^{1/2} \xi \\ \approx -3 \frac{A^2C}{\lambda^{5/2} a^3} \int_0^{\infty} \frac{\xi d\xi (\tan^{-1}\xi)^2}{(1 + \xi^2)^{5/2}} = -0.54 A^2 C \lambda^{-5/2} a^{-3} \quad . \quad (\text{B8})$$

Maximization of I with respect to A and a then gives

$$A = \frac{\Delta M(0) V_0}{s + \Gamma} \quad , \quad (\text{B9})$$

with

$$\Gamma = (8D_{\parallel}a + 0.54C\lambda^{-5/2}a^{-3}) V_0^{-1} \quad (\text{B10})$$

and

$$a = (3 \times 0.54/8)^{1/4} (C/D_{\parallel})^{1/4} \lambda^{-5/8} = 0.67 (C/D_{\parallel})^{1/4} (D_{\perp}/D_{\parallel})^{5/8} \quad . \quad (\text{B11})$$

By inserting the value of a (B11) into (B10) and noting that $V_0^{-1} = N\lambda = N(D_{\perp}/D_{\parallel})$ from Eq. (25), we obtain

$$\Gamma = 7.2NC^{1/4}(D_{\parallel}D_{\perp})^{3/8} \quad . \quad (\text{B12})$$

*Sandia Laboratories is a U. S. Department of Energy facility.

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