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Theory of Chemically Induced Dynamic Polarization in Thin Films*

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An analysis is presented for radical recombination according to a continuous diffusion model for two and three dimensional systems in the context of chemically induced dynamic polarization (CIDNP) experiments. It is argued that diffusional models of molecular motion are most sensitive to changes in dimensionality and that CIDNP or other experiments carried out in thin film, quasi-two dimensional systems, should reveal these effects. The reason for this sensitivity is that according to a diffusion model dynamical quantities of interest will decay more slowly in two dimensions rather than three. We discuss how these conclusions apply to a variety of experiments and two additional examples are cited.

I. INTRODUCTION

In 1967 Fischer, Bargon, and Johnson[1] and, independently, Ward and Lawler[2] reported anomalous nuclear magnetic resonances intensity patterns in the spectra of the products of reactions in which intermediate radical pairs are involved. The basic mechanism for this effect, called "chemically induced dynamic polarization" (CIDNP), is the singlet-triplet mixing that occurs in the intermediate radical pair for the brief time period between radical formation and recombination. The important features of this mechanism were first worked out by Closs,[3] and independently, Kaptein and Oosterhoff.[4] One assumes that the radicals are initially formed at an appreciable separation r_0 in an electronic singlet or triplet state. The radicals wander about for a time during which the Zeeman and hyperfine interactions cause mixing between the singlet and triplet electronic states that are separated by a scalar exchange coupling $2J$, assumed constant. Recombination takes place with probability λ, when the radical pair becomes separated by a critical distance a, $a<r_0$, provided the radical pair is in a singlet state.

The central quantity of interest for the interpretation of CIDNP experiments is the probability of forming cage products, which may be written[5] as

$$w^{(i)}=\lambda\int_0^\infty [C_s^{(i)}(t)]^2 f(t)\,dt, \qquad i=s,t. \tag{1.1}$$

In this expression $[C_s^{(i)}(t)]^2$ is the probability that the radical pair is a singlet at time t, given that, at time zero the pair was a singlet $i=s$ or a triplet $i=t$. The quantity $f(t)$ is the probability that the radical pair initially formed at separation r_0 will be at time t at separation *a for the first time.* While it is not explicitly indicated, $C_s^{(i)}(t)$ and hence $w^{(i)}$ depend on the nuclear spin states of both radical fragments. Clearly evaluation of $w^{(i)}$ depends on calculation of both $C_s^{(i)}(t)$ and $f(t)$. The calculation of the amplitudes $C_s^{(i)}(t)$ presents no serious problems (see Sec. II).

It remains to compute the dynamical probability factor $f(t)$. Early formulations[3,4] arbitrarily adopted an exponential form for $f(t)$ which has proven only moderately successful.[5] In an elegant series of papers Adrian[6] proposed that a diffusion model would be a

more realistic way to determine $f(t)$. In particular Adrian employed the constant step random flight model of Noyes[7] to compute $f(t)$ and hence $w^{(i)}$. It appears that this step diffusion model is more successful at predicting the observed intensity patterns than the simple exponential model.

Here we wish to emphasize that CIDNP measurements may be used to study how a pair of radicals move about in solution; that is CIDNP is a probe for the dynamical probability factor $f(t)$. In particular the characteristic time of geminate recombination is usually thought to occur in a time of 10^{-9}–10^{-10} sec, a time scale on which the model of step diffusion or ordinary continuous diffusion might well be suspect. It occurred to us that the predictions of diffusion type models are most sensitive not to changes in temperature or density, etc., but, to put it bluntly, changes in dimensionality. The underlying reason for this is that diffusion (or random walk) type trajectories always return to the neighborhood of the origin in two dimensions but not in three dimensions. The consequence of this in a variety of physical situations is that the temporarl decay of quantities of interest, such as $f(t)$, will be much slower in two dimensions than in three dimensions. The purpose of this paper is to present an analysis for CIDNP in two dimensions. We fine it convenient to describe the diffusion of two radicals relative to one another by a continuous diffusion model rather than the step diffusion model employed by Adrian.[6–8] The continuous diffusion model is analytically more tractable than the step diffusion model, leads to essentially identical results for w, and, so far as we are aware, does not do substantially more violence to the underlying physical process. In Sec. II we summarize the result of previous theories and in Sec. III we present the results of the continuous diffusion model for two and three dimensional systems.

We are perfectly aware that strictly two dimensional systems do not exist in nature. Adsorbed layers and very thin films always will have an effective depth L. In addition there may be present completely different mechanisms, such as interactions with adjoining phases, that compromise the assumed two dimensional character of a system. Ultimately one must rely on experiments on real quasi-two dimensional systems to reveal the sorts of effects that are discussed here. We have treated analytically the limiting two dimensional case where the effects are most pronounced. We have not treated the more realistic case of a layer of finite thickness because of the analytic complexity. In a layer of finite thickness a portion of the diffusion (or random walk) trajectories will also be strongly perturbed from the three dimensional case and the effects discussed for the two dimensional case will appear, but in a more muted way. In the final section where we discuss other experiments that have a strong dimensionality dependence due to diffusive motion, we present a qualitative assessment of how thin a system must be in order to see appreciable deviations from three dimensional predictions.

Many experiments are interpreted on the basis of a diffusion model for molecular motion. The reader should keep in mind that our basic motivation is to encourage experimentalists to consider, in the context of their measurements, the study of quasi-two dimensional systems as a means of testing these models.

We do not wish to suggest that difficulties will not be encountered in designing an unambiguous quasi-two dimensional CIDNP experiment. For example in a thin film the number of spins available for observation is low and increasing the concentration may only serve to reduce the importance of the geminate recombination pathway. Furthermore different reaction and relaxation mechanisms may come into play at the boundary which could make the experimental interpretation difficult. However, these difficulties should not obscure the fact that an interesting experiment is possible.

II. BACKGROUND FOR THE CALCULATION

Although we shall not present the details here,[3–8] it is an easy matter to arrive at expressions for $C_s^{(i)}(t)$ based on a reasonable quantum mechanical model for the radical pair. The Hamiltonian one adopts is

$$H=\beta_0[g_1S_1^{(z)}+g_2S_2^{(z)}]H_0-J(2\mathbf{S}_1\cdot\mathbf{S}_2+\tfrac{1}{2}) + \sum_\alpha A_{1\alpha}I_\alpha^{(z)}S_1^{(z)}+\sum_\beta A_{2\beta}I_\beta^{(z)}S_2^{(z)}, \quad (2.1)$$

where β_0 is the Bohr magneton, H_0 the external magnetic field in the z direction, g_1 and g_2 are the electronic g factors of radicals 1 and 2, respectively, and $A_{1\alpha}(A_{2\beta})$ are the hyperfine coupling constants between nucleus $\alpha(\beta)$ of spin $I_\alpha(I_\beta)$ on radical 1 (2). For simplicity only the z component of the isotropic hyperfine coupling is retained. One seeks a solution of the form

$$\psi(t)=[C_s(t)\mid S\rangle+C_t(t)\mid T_0\rangle]\chi_n, \quad (2.2)$$

where χ_n is an appropriate nuclear spin function and again for simplicity, mixing with the other electronic triplet components. $T_{\pm1}$ is neglected. If the pair is initially a singlet $C_s(0)=1$ the solution for $[C_s^{(s)}(t)]^2$ is

$$[C_s^{(s)}(t)]^2=1-(\omega_n^2/\omega^2)\sin^2\omega t, \quad (2.3)$$

while if the pair is initially a triplet $C_t(0)=1$ the solution for $[C_s^{(t)}(t)]^2$ is

$$[C_s^{(t)}(t)]^2=(\omega_n^2/\omega^2)\sin^2\omega t. \quad (2.4)$$

In Eqs. (2.3) and (2.4)

$$\omega_n=(H_0\beta_0/2)(g_1-g_2)+\tfrac{1}{2}[\sum_\alpha A_{1\alpha}m_\alpha^{(1)}-\sum_\beta A_{2\beta}m_\beta^{(2)}] \quad (2.5)$$

and

$$\omega=[J^2+\omega_n^2]^{1/2}, \quad (2.6)$$

where $m_\alpha^{(1)}(m_\beta^{(2)})$ are the spin quantum states of nu-

cleus α (β) of radical 1 (2). The set of Eqs. (2.3)–(2.6) determine the quantum mechanical probabilities $[C_s^{(i)}(t)]^2$ appearing in the expression for $w^{(i)}$, Eq. (1.1). We next turn to consideration of the dynamical probability factor $f(t)$.

If one adopts an exponential form for $f(t)$,[3,4]

$$f(t)=\tau^{-1}\exp(-t/\tau), \tag{2.7}$$

one obtains the following expressions for the probability w:

$$w_{\exp}^{(t)}=2\lambda(\omega_n\tau)^2/[1+(2\omega\tau)^2] \tag{2.8}$$

and

$$w_{\exp}^{(s)}=\lambda\{1-2(\omega_n\tau)^2/[1+(2\omega\tau)^2]\}. \tag{2.9}$$

For large magnetic fields such that $\omega\sim\omega_n$ and for $\omega\tau\ll1$, these expressions predict that the probabilities depend on the square of the magnetic field.

Adrian employed the Noyes step-diffusion model[9] to determine $f(t)$. For the first re-encounter (to which we restrict attention here) the numerical results of Noyes for $f(t)$ may be put in the form

$$f_s(t)=0, \qquad t<2\tau$$
$$f_s(t)=(0.24/\tau)[(t/\tau)+0.44]^{3/2}, \qquad t\geq2\tau, \tag{2.10}$$

where τ is the time between diffusive jumps. The dynamical probability factor $f(t)$ is zero for times less than 2τ because one assumes that the radicals are initially formed at a separation of two diffusive steps and so cannot recombine in a time less than 2τ. Adrian shows[6–8] that in the limit $\omega\tau\ll1$ this form of $f(t)$ leads to the following expressions for w:

$$w_{\text{step}}^{(t)}=\lambda(\omega_n/\omega)^2(0.24)(\pi\omega\tau)^{1/2} \tag{2.11}$$

and

$$w_{\text{step}}^{(s)}=\lambda(0.24)[2(2.44)^{-1/2}-(\omega_n/\omega)^2(\pi\omega\tau)^{1/2}]. \tag{2.12}$$

For large magnetic fields $\omega\sim\omega_n$ these expressions predict a dependence on the square root of the magnetic field.

III. CALCULATION OF THE DYNAMICAL PROBABILITY FACTOR

In this section we present a calculation for $f(t)$ in two and three dimensional systems by use of a continuous diffusion model. The dynamical probability factor $f(t)$ is the probability that two radicals initially separated by a distance r_0 will arrive for the first time at separation $a<r_0$ between t and $t+dt$. The two radicals are assumed ro move about *independently* by diffusion. Consequently the probability of finding the two radicals at relative separation $\mathbf{r}$ between t and $t+dt$ is given by the diffusion equation

$$\partial P_d(\mathbf{r},t)/\partial t=D\nabla_r^2P_d(\mathbf{r},t), \tag{3.1}$$

where D is the sum of the diffusion coefficients for the two radicals. Here the Laplacian and $\mathbf{r}$ take a form appropriate to two or three dimensions, $d=2$ or 3, respectively. For an arbitrary initial distribution $P_d(\mathbf{r},0)$, Eq. (3.1) has the formal solution ($d=2, 3$)

$$P_d(\mathbf{r},t)=\exp[D\nabla_r^2t]P_d(\mathbf{r},0). \tag{3.2}$$

We shall restrict attention to a special class of initial conditions which do not depend on orientation

$$P_d(\mathbf{r},0)=[F(r)/\pi2^{d-1}]. \tag{3.3}$$

Normalization requires

$$\int_0^\infty r^{d-1}F(r)\,dr=1. \tag{3.4}$$

For this class of initial conditions

$$P_d(r,t)=\exp[L_d(r)t][F(r)/\pi2^{d-1}], \tag{3.5}$$

where

$$L_3(r)=D[(1/r^2)(d/dr)r^2(d/dr)], \tag{3.6}$$

or

$$L_2(r)=D[r^{-1}(d/dr)r(d/dr)]. \tag{3.7}$$

The solution, Eq. (3.5), may be expressed as

$$P_d(r,t)=\int_0^\infty r_0^{d-1}G_d(r,t\mid r_0,0)F(r_0)\,dr_0, \tag{3.8}$$

where the Green's function $G_d(r,t\mid r_0,0)$ is defined by

$$G_d(r,t\mid r_0,0)=\exp[L_d(r)t][\delta(r-r_0)/(2r_0)^{d-1}\pi]. \tag{3.9}$$

This Green's function has the interpretation of the probability of finding a separation between $r+dr$ at time t given an initial separation in the infinitesimal radial shell about r_0. The Green's function satisfies the equation

$$\partial G_d(r,t\mid r_0,0)/\partial t=L_d(r)G_d(r,t\mid r_0,0) \tag{3.10}$$

with initial condition

$$G_d(r,0\mid r_0,0)=[\delta(r-r_0)/\pi(2r_0)^{d-1}]. \tag{3.11}$$

The quantity we seek, $f_d(t)$ ($d=2, 3$), is closely related to G_d. The Green's function gives the probability of separation r at time t irrespective of how often the separation r has been realized during prior times. On the other hand we require $f_d(t)$, the probability that a particular separation a is achieved at time t for the first time given that the initial separation was $r_0>a$. This probability distribution for first arrival times is required for interpretation of the CIDNP experiment because it is imagined that the radicals form diamagnetic products with high efficiency ($\lambda\sim1$) once they approach a distance a. If required recollisions may also be included.

A well-known trick is available[8] for finding $f_d(t)$ from G_d. Essentially one solves Eq. (3.10) subject to an absorbing boundary condition at $r=a$,

$$G_d(a,t\mid r_0,0)=0, \tag{3.12}$$

which has the effect that a particle remains at separation $r=a$ after its arrival. It follows that the flux of probability at $r=a$ is precisely the first arrival prob-

ability density $f_d(t)$. Thus

$$f_d(t)=\pi D(2a)^{d-1}\left[\frac{dG_d(r,\,t\mid r_0,0)}{dr}\right]_{r=a}, \quad (3.13)$$

when G_d is the solution to Eq. (3.10) on the interval $a<r<\infty$ with initial condition Eq. (3.11) and boundary conditions Eq. (3.12) and

$$\lim_{r\to\infty} G_d(r,\,t\mid r_0,0)\to 0. \quad (3.14)$$

If one wishes to find the probability density for first arrival times for a particular initial distribution $F(r_0)$ one needs only average $f_d(t)$ in Eq. (3.13) with this distribution.

The Green's functions G_2 and G_3 may be found by eigenfunction expansion or other methods.[9] We present in turn the results for two and three dimensions.

For three dimensions

$$G_3(r,\,t\mid r_0,0)=[2\pi^2 r r_0]^{-1}\int_0^\infty dk\,\exp(-Dk^2t)\times\sin[k(r_0-a)]\sin[k(r-a)] \quad (3.15)$$

or

$$G_3(r,\,t\mid r_0,0)=(4\pi^2 r r_0)^{-1}(\pi/4Dt)^{1/2}\times\{\exp[-(r-r_0)^2/4Dt]-\exp[-(r+r_0-2a)^2/4Dt]\}, \quad (3.16)$$

which leads, according to Eq. (3.13), to the following expression for $f_3(t)$:

$$f_3(t)=[Da(r_0-a)/2\pi^{1/2}r_0(Dt)^{3/2}]\exp[-(r_0-a)^2/4Dt]. \quad (3.17)$$

Note that

$$f_3(t)\sim t^{-3/2} \quad \text{as} \quad t\to\infty \quad (3.18)$$

and that

$$\int_0^\infty f_3(t)\,dt=\frac{a}{r_0}. \quad (3.19)$$

The asymptotic expression for $f_3(t)$ is similar to the step diffusion result $f_s(t)$, Eq. (2.10). Furthermore Eq. (3.19) states that in three dimensions the probability that the two radicals will never reach a separation a is $(1-a/r_0)$. From Eqs. (1.1), (2.3), (2.4), and (3.17) we may compute for the three dimensional continuous diffusion model, the probability of forming cage products, w. The result is

$$w_3^{(t)}=(\lambda\omega_n^2 a/2\omega^2 r_0)[1-e^{-p}\cos(2p)] \quad (3.20)$$

and

$$w_3^{(s)}=\lambda\{(a/r_0)-(\omega_n^2 a/2\omega^2 r_0)[1-e^{-p}\cos(2p)]\}, \quad (3.21)$$

where

$$p=(r_0-a)(\omega/8D)^{1/2}. \quad (3.22)$$

For three dimensional diffusion[10]

$$D=(a^2/6\tau), \quad (3.23)$$

where τ is the time between diffusive jumps so that

$$p=[(r_0/a)-1](3\omega\tau/4)^{1/2}. \quad (3.24)$$

Since $\omega\tau\ll 1$, one may take the small p limiting forms of Eq. (3.20) and (3.21),

$$w_3^{(t)}=\lambda(\omega_n^2/\omega^2)[1-(a/r_0)](\sqrt{3}/4)(\omega\tau)^{1/2} \quad (3.25)$$

and

$$w_3^{(s)}=\lambda\{(a/r_0)-[(\omega_n^2/\omega^2)[1-(a/r_0)](\sqrt{3}/4)(\omega\tau)^{1/2}]\}. \quad (3.26)$$

These results for the continuous diffusion model agree quite well with Adrian's results for the step diffusion model. For large magnetic fields a square root dependence on the magnetic field is predicted and the numerical coefficients are quite close with the choice $r_0=2a$.

The two dimensional analysis is slightly more complicated because not all the necessary integrals can be performed analytically. The Green's function is

$$G_2(r,\,t\mid r_0,0)=(2\pi)^{-1}\int_0^\infty dk k\,\exp(-Dk^2t)\times\frac{C_0(kr)C_0(kr_0)}{Y_0^2(ka)+J_0^2(ka)}, \quad (3.27)$$

where

$$C_0(kr)=J_0(kr)Y_0(ka)-J_0(ka)Y_0(kr), \quad (3.28)$$

and $J_0(x)$ and $Y_0(x)$ are zeroth order Bessel functions of the first and second kind, respectively. From Eq. (3.13) it follows that

$$f_2(t)=\frac{-2D}{\pi}\int_0^\infty dk k\,\exp(-Dk^2t)\,\frac{C_0(kr_0)}{Y_0^2(ka)+J_0^2(ka)}. \quad (3.29)$$

The long time asymptotic behavior of $f_2(t)$ may be determined by the substitution $x=Dk^2t$ in Eq. (3.29),

$$f_2(t)=-(\pi t)^{-1}\int_0^\infty dx e^{-x}C_0\left[\left(\frac{x}{Dt}\right)^{1/2}r_0\right]\times\left\{Y_0^2\left[\left(\frac{x}{Dt}\right)^{1/2}a\right]+J_0^2\left[\left(\frac{x}{Dt}\right)^{1/2}a\right]\right\}^{-1} \quad (3.30)$$

followed by evaluation of the integral when C_0, Y_0, and J_0 are replaced by their limiting form for small argument. The result is

$$f_2(t)\sim\ln(r_0/a)(2/t)[\ln(\tau/t)]^{-2}, \quad (3.31)$$

where we have made the identification[10]

$$D=(a^2/4\tau) \quad (3.32)$$

appropriate to two dimensional diffusion. While the integral in Eq. (3.29) cannot be easily performed, it can be shown[11] that

$$\int_0^\infty f_2(t)\,dt=1. \quad (3.33)$$

For two dimensions Eqs. (3.31) and (3.33) show that the two radicals will always achieve the critical separation and that the time decay of the dynamical probability factor is much slower in two dimensions than in three.

In order to compute the probability of forming cage products in two dimensional systems, w_2, one must perform integrals of the type

$$\int_0^\infty f_2(t)\,\sin^2\omega t dt = \frac{-4}{\pi}\int_0^\infty \frac{dk}{k}\frac{\omega^2}{[(Dk^2)^2+(2\omega)^2]} \times\{C_0(kr_0)[Y_0^2(ka)+J_0^2(ka)]^{-1}\}. \quad (3.34)$$

This integral may be evaluated approximately in the limit

$$\omega\tau=\omega a^2/4D\ll 1 \quad (3.35)$$

with the result

$$\int_0^\infty f_2(t)\,\sin^2\omega t dt=\tfrac{1}{2}\ln\left(\frac{r_0}{a}\right)\{\ln[(\omega\tau)^{-1/2}]\}^{-1}. \quad (3.36)$$

It follows from Eqs. (1.1), (2.3), and (2.4) that

$$w_2^{(t)}=\lambda(\omega_n^2/\omega^2)\tfrac{1}{2}\ln(r_0/a)\{\ln[(\omega\tau)^{-1/2}]\}^{-1} \quad (3.37)$$

and

$$w_2^{(s)}=\lambda-\lambda(\omega_n^2/\omega^2)\tfrac{1}{2}\ln(r_0/a)\{\ln[(\omega\tau)^{-1/2}]\}^{-1}. \quad (3.38)$$

In contrast to the three dimensional case there is a logarithmic dependence on the magnetic field when $\omega\sim\omega_n$. Thus the striking difference between the two and three dimensional systems for the CIDNP experiment is the magnetic field dependence of w. In addition there will be a substantially modified temperature dependence of w arising from the temperature dependence of τ.

IV. DISCUSSION

Our calculation clearly indicates the striking differences that may be expected from CIDNP carried out in two and three dimensional systems. We next wish to formulate and discuss the qualitative criterion necessary for a real system to behave as a quasi-two dimensional system. Essentially this criterion is that a representative trajectory of a radical must encounter the boundary of the system several times before recombination. For an infinite layer of thickness L this criterion is

$$L<(6Dt_c)^{1/2}=a(t_c/\tau)^{1/2}, \quad (4.1)$$

where t_c is the observed time constant for recombination. Since the best estimate[12] of t_c is approximately 10^{-10} sec and τ and a are roughly 10^{-12} sec and 2 Å, respectively, once L is less than 20 Å the two dimensional character of the film should emerge. It should be noted that much larger values of t_c have been estimated.[13] It should be possible to realize films of this thickness or less in a variety of experiments.

It is possible to estimate t_c within the framework of the theory. Ordinarily one would identify t_c with

$$\bar{t}=\int_0^\infty tf_3(t)\,dt \quad (4.2)$$

but this integral does not exist. Alternatively one may identify t_c with the most probable value t_0 of $f_3(t)$,

$$t_0=[(r_0-a)/a]^2\tau. \quad (4.3)$$

If t_0 is taken to be 10^{-10} sec and $\tau=10^{-12}$ sec a value of r_0 roughly equal to $10a$ is implied. This value of the initial separation is much larger than is thought reasonable for a radical formation. Normally one assumes that r_0 is about $2a$ which implies that t_c should be about 10^{-12} sec in contrast to the observed value of 10^{-10} sec or longer. We believe the resolution of this problem is as follows. Radical formation occurs at $r_0\sim a$. In the first brief period of time ($\sim 10^{-12}$ sec) the radicals may recombine or an event unfavorable for recombination may happen. The unfavorable event might be, for example, the interposition of one or two solvent molecules or rotation of one radical fragment. The radical pairs that experience this unfavorable event may be treated as if they had an effective initial separation much larger than $r_0=a$. The implication of this view is that, on a fast enough time scale, two time constants for geminate recombination should be observed.

In this paper we have given a detailed analysis of the CIDNP experiment in two and three dimensions. Other experiments are interpreted on the basis of molecular diffusion and these should also be candidates interesting quasi-two dimensional measurements. We discuss briefly two examples.

First, elegant picosecond spectroscopy experiments are underway[12] to observe directly the time decay of radical fragments formed by photolysis. These experiments are more powerful than CIDNP in the sense that the probability of recombination is observed directly as a function of time. For geminate recombination, if the efficiency for product formation is high, $\lambda\sim 1$, the picosecond experiment should measure $f_d(t)$ directly. Experiments carried out in films of variable thickness should show a transition between $f_3(t)$ and $f_2(t)$. If the efficiency for product formation is smaller, the measured quantity for geminate recombination, $F_d(t)$, is the probability of product formation taking into account that prior arrivals at separation a did not lead to products. The quantity $F_d(t)$ may be bound from the integral equation

$$F_d(t)=\lambda f_d(t)+(1-\lambda)\int_0^t ds f_d(t-s)F_d(s). \quad (4.4)$$

As a second example we consider nuclear magnetic relaxation by intermolecular dipolar coupling. For this sort of relaxation mechanism it is usual to evaluate the correlation functions one encounters by the continuous diffusion model.[14] These correlation functions have the

form

$$k_{lm}(t) = (N-1)\langle\{Y_{lm}^*[\Omega(t)]/r^3(t)\}\{Y_{lm}[\Omega(0)]/r^3(0)\}\rangle, \quad (4.5)$$

where Y_{lm} is a spherical harmonic, r is the distance between two representative spins, and Ω denotes the orientation of $\mathbf{r}$ with respect to the external magnetic field. The calculation of $k_{lm}(t)$ for a three dimensional system according to the continuous diffusion model is well known[14]; the correlation functions decay rapidly in time, their Fourier transforms exist at all frequencies, and well behaved values of T_1 and T_2 result.

In a two dimensional system qualitatively new effects appear. This problem has been considered in some detail by Kokin and Izmest'ev.[15] First one must relate the spherical harmonics defined with respect to the external magnetic field to spherical harmonics defined with respect to an axis perpendicular to the two dimensional surface. Next the correlation functions must be evaluated according to the two dimensional diffusion equation. For the case $l=2$ one finds

$$k_{lm}(t) = (5\rho/2)\{|\, d_{0m}^{(2)}(\beta)\,|^2 K_0(t) + \tfrac{3}{8}[|\, d_{-2m}^{(2)}(\beta)\,|^2 + |\, d_{2m}^{(2)}(\beta)\,|^2]K_2(t)\}, \quad (4.6)$$

where

$$K_n(t) = \int_0^\infty dk k \exp(-Dk^2t)\left[\int_a^\infty dr J_n(kr) r^{-2}\right]^2, \quad (4.7)$$

$d_{nm'}^{(l)}(\beta)$ is a matrix element of a finite rotation[16] and β is the angle the external magnetic field makes with the axis perpendicular to the slab. Note the strong dependence on the angle β.

An alternative expression for $K_n(t)$ is[17]

$$K_n(t) = \int_a^\infty dr \int_a^\infty dr_0[r^2 r_0^2 2Dt]^{-1} \times \exp[-(r^2+r_0^2/4Dt)]I_n(rr_0/2Dt), \quad (4.8)$$

where $I_n(x)$ is the modified Bessel function. From this formula it may be shown that $K_0(t)$ has the slow asymptotic time dependence t^{-1}. It follows that for the two dimensional system the correlation function $k_{lm}(t)$ will not decay fast enough for the zero frequency Fourier transforms to exist. In short the normal condition for motional narrowing are not present and the intermolecular magnetic relaxation must be interpreted by techniques usually employed for slow motion in solids. We believe that such effects should be observable in thin liquid films or absorbed layers.

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