Phase relaxation in a many-body system of diffusing spins: Slow motional limit

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The echo amplitude decay of a diffusing electron-spin-bearing molecule interacting with a diffusing many-spin bath of proton-containing molecules has been studied theoretically in the slow motional limit. Closed-form asymptotic expressions for the short- and long-time behavior of the echo envelope have been obtained. In contrast to the well-studied fast-motional limit, the echo envelope cannot be described by a simple exponential decay, and its rate exhibits a $D_T^{1/3}$ dependence on the relative translational diffusion coefficient, D_T. For low proton concentrations and long pulse delay times, τ, an exponential $\tau^{9/8}$-decay of the echo amplitude is found, whereas for high proton concentrations and short τ's the decay exhibits an exponential τ^3-behavior. These limiting analytical results are compared with the exact numerical solutions to establish their range of validity. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1481764]

I. INTRODUCTION

In the fast motional limit, the classic theories of spin relaxation used in NMR and ESR in fluid media have been available for many years.[1] These theories are formulated for the rotational diffusion of a single spin-bearing molecule or else the relative translational diffusion of a pair of spin-bearing molecules. These approaches are perturbational in nature, based on the rapid stochastic modulation of the dipolar and other interaction tensors by the motion. In viscous media (slow motions) the conventional motional narrowing theories are no longer valid, and a full solution to the stochastic modulation of the spin dependent interactions must be employed. The usual slow motional spin relaxation analyses for these cases are based on the stochastic Liouville equation (SLE).[2] Their relevance is well established for a wide range of ESR (and also NMR) experiments.[2,3] However, these one- or two-body motional modulation cases do not adequately address the case of many spin-bearing molecules simultaneously interacting by their dipolar interactions, while they are separately diffusing. In the motional narrowing (or Redfield) regime, Torrey developed a successful *ad hoc* model,[4] which is appropriate for dilute solutions. In this model, the many-body effects were taken into account by a simple multiplication of the inverse relaxation times T_1^{-1} or T_2^{-1} for a pair of interacting spins by the number density. However, when the motions slow down sufficiently, then the many-body interactions persist for long times and the Torrey approach does not generalize to the slow motional regime.

Recently, we have developed a many-body theory for spin relaxation to address this general issue. We showed that under the assumption of statistical independence of the motions, it is possible to express the time evolution of the many-body free induction decay or echo decay as a general function of the two-body solution,[5] cf. below, and the latter is solved using the SLE.[6] The numerical results obtained recover the Torrey–Redfield results in the motional narrowing regime and also give the correct result, known as Anderson's statistical theory[1,7,8] in the limit of a dilute solid, as well as a full description of the intermediate regime between these two limits.

In one of our recent contributions,[9] two channels for the relaxation of an electron- spin in a many-spin bath of protons have been studied. The first is spin diffusion, which predominantly governs the relaxation in the rigid limit. This yields an echo amplitude decay that is quadratic in time in the exponential due to the presence of flip-flop terms in the homonuclear proton part of the Hamiltonian.[9] When motions occur, a dephasing arises, which is due to the translational diffusion of the protons relative to that of the electron spin. This latter dephasing becomes comparable with spin diffusion even for ultraslow motional rates, i.e., when the diffusion coefficient for relative motion is less than $D_T = 10^{-12}$ cm^2/s. The echo envelope due to such a diffusional dephasing has been studied so far only numerically.[5,9,10]

What has been lacking is an analytical closed-form result appropriate for the slow motional regime to provide the insight not readily obtainable from the numerical solutions. It is the purpose of this article to report on this analytic solution appropriate for very slow motions and to demonstrate its range of validity by comparison with the full numerical results. We describe the new insights provided with respect to the nonexponential decay of the phase memory in spin echo experiments. These results are especially relevant to ESR experiments in viscous media such as liquid crystals and glass forming fluids,[5,9,11,12] as well as NMR in polymers and solids.[13,14]

The case that we explicitly consider is relaxation of a single spin with a large magnetic moment (e.g., an electron

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spin) in the field of many diffusing spins with weak magnetic moments (e.g., protons). For this case we are able to start with the fundamental general result previously derived [cf. Eq. (2.3)].[5,9] This general result also applies to another case, that of many identical spins, each diffusing independently. Thus the present approach also applies to this second case, but it is complicated by other factors (viz. the generation of multi-quantum coherences,[11] which can in principle be suppressed by using magic echo techniques). Thus our results are presented in the context of the first case.

II. ENSEMBLE-AVERAGED SOLUTION TO THE ECHO SIGNAL IN THE PRESENCE OF MOTIONS

We start by employing the expression for the echo signal, $G(t)$ of an electron spin (S) interacting with a dynamical bath of N identical protons [$I^{(i)}$], which is obtained from solving the von Neumann equation for the many-spin density matrix in Liouville or superoperator form:[5,9]

$$\frac{G(t)}{Z}=\mathbf{g}^{\mathbf{T}}(0)\left\langle e_{\mathrm{O}}^{-i\int_{\tau}^{t}dt_2\mathbf{H}^{x}(t_2)}\mathbf{X}_{\pi_x}e_{\mathrm{O}}^{-i\int_{0}^{\tau}dt_1\mathbf{H}^{x}(t_1)}\right\rangle\mathbf{g}(0)$$

$$=\mathbf{g}^{\mathbf{T}}(0)\langle e_{\mathrm{O}}^{-i\int_{\tau}^{t}dt_2\mathbf{H}^{x}(t_2)}e_{\mathrm{O}}^{-i\int_{0}^{\tau}dt_1\tilde{\mathbf{H}}^{x}(t_1)}\rangle\mathbf{X}_{\pi_x}\mathbf{g}(0), \tag{2.1}$$

which is Eq. (5.5) in Ref. 9. Also[15] $\tilde{\mathbf{H}}^{x}(t)\equiv\mathbf{X}_{\pi_x}\mathbf{H}^{x}(t)\mathbf{X}_{\pi_x}^{-1}$. In Eq. (2.1) the vector $\mathbf{g}(0)$ describes the many-spin density state immediately after the initial $(\pi/2)_x$ pulse. It corresponds to a representation of the density matrix in Liouville space, which is defined by the Frobenius trace metric [cf. Eq. (2.8) in Ref. 5]. $\mathbf{H}^{x}$ and $\mathbf{X}$ are the rotating frame Hamiltonian and pulse superoperators, respectively, Z is a normalization constant, and the angular brackets imply ensemble averaging.

The spin Hamiltonian that is appropriate for this slow-motional case of a single A (electron) spin interacting with N spins of type B (protons) is[9]

$$H=\sum_{i=2}^{N+1}\chi_0F_0(\mathbf{r}_{1i})S_zI_z^{(i)}+\chi_1[F_{-}(\mathbf{r}_{1i})S_zI_{+}^{(i)}$$

$$+F_{+}(\mathbf{r}_{1i})S_zI_{-}^{(i)}]. \tag{2.2}$$

As usual, the nonsecular electron spin-flip terms have been neglected in Eq. (2.2), since they are not important, except for very fast motions.[2] Whereas the pseudo-secular $S_zI_{\pm}$ terms are, in general, significant, they were found in the numerical solutions to be unimportant for the very slow motional range over which the asymptotic solutions to be obtained in Sec. III are valid (except for very weak echo-envelope modulation).[9] Thus we shall neglect them below. We shall also neglect the additional relaxation by spin diffusion, or assume that it is suppressed by other means (e.g., the motional averaging[9] or by proton spin-locking at the magic angle). Now if the motions of the spins are assumed to be stochastically independent, the echo signal is given by[5,9] [cf. the closely related case given by Eqs. (6.15) of Ref. 5]

$$G(t)=2^{-(N+1)}q\left\langle\exp\left[-i\frac{\chi}{2}\int_0^t dt_1s(t_1)F(\mathbf{r}(t_1))\right]\right.$$

$$\left.+\exp\left[i\frac{\chi}{2}\int_0^t dt_1s(t_1)F(\mathbf{r}(t_1))\right]\right\rangle^{N}, \tag{2.3}$$

where $q=\hbar\omega/kT$, $\chi\equiv\chi_0=\sqrt{(16\pi/5)}\gamma_A\gamma_B\hbar$ is the coupling constant, and the $\mathbf{r}$-dependent functions (containing the implicit time dependence) are given in terms of the spherical harmonic of rank two, $F(\mathbf{r})\equiv F_0(\mathbf{r})=Y_0^{(2)}(\theta,\phi)/r^3$. The s-function is given by $s(t)=+1$, $t>\tau$, and $s(t)=-1$, $t<\tau$.

In the thermodynamic limit of a very large number of spins, N, and a large volume, V, the Markov method[16] can be applied to Eq. (2.3), which yields[5,9]

$$G(t)=G(0)\exp\left[C\int_0^t dt_1\frac{\partial g(t_1)}{\partial t_1}\right], \tag{2.4}$$

where $C=N/V$ is the concentration of the matrix protons in the present case. Also, $g(t)\equiv[g_{+}(t)+g_{-}(t)]/2$ and the two-body spin-echo signal from the S spin interacting with a single I spin is given by

$$g_{\pm}(t_1)\equiv\left\langle\exp\left[\mp i\frac{\chi}{2}\int_0^{t_1}dt_2s(t_2)F(\mathbf{r}(t_2))\right]\right\rangle'. \tag{2.5}$$

[In Eq. (2.5), the prime means that the volume has already been factored out.[5]] The motionally path-averaged components $g_{\pm}(t)$ are found from the solution of the SLE[2] for the auxiliary function $g_{\pm}(\mathbf{r},t)$:

$$\frac{\partial g_{\pm}(\mathbf{r},t)}{\partial t}-D_T\nabla^2g_{\pm}(\mathbf{r},t)=\mp i\frac{\chi}{2}F(\mathbf{r})s(t)g_{\pm}(\mathbf{r},t), \tag{2.6}$$

where we have $g_{\pm}(t)=\int d^3\mathbf{r}\,g_{\pm}(\mathbf{r},t)$. Here D_T is the relative translational diffusion coefficient for a pair of interacting spin-bearing molecules (i.e., a proton-bearing and an electron-spin-bearing molecule), which is given by the sum of their respective diffusion coefficients. The initial condition is given by $g_{\pm}(\mathbf{r},0)=p_{\mathrm{eq}}(\mathbf{r})$, the equilibrium probability distribution. For the two-body echo signal, $g_{\pm}(t)$, one can formally write the solution of Eqs. (2.5) and (2.6) as

$$g_{\pm}(t)=\int\mathbf{d}^3\mathbf{r}\,e^{[\mp i(\chi/2)F(\mathbf{r})+D_T\nabla^2](t-\tau)}$$

$$\times e^{[\pm i(\chi/2)F(\mathbf{r})+D_T\nabla^2]\tau}p_{\mathrm{eq}}(\mathbf{r}). \tag{2.7}$$

In summary, we have, under the assumption of stochastic independence of the diffusion of the spin-bearing molecules, that the echo decay in the many-body case is an analytic function of that for the two-body problem.

III. ASYMPTOTIC EXPANSIONS OF THE ECHO BEHAVIOR

We now seek asymptotic expressions that are valid in the limit of very slow motions. The other limit of motional narrowing can readily be obtained from Eq. (2.3) as discussed previously[5,9] by utilizing generalized cumulant expansions

and truncations after the second order. This approach does not yield a satisfactory method for the slow motional limit, so we must proceed in a different manner.

For $t=2\tau$ we first use the following exact property of noncommuting symmetric operators **A** and **B** (cf. the Appendix):

$$e^{(\mathbf{A}+\mathbf{B})\tau}e^{(-\mathbf{A}+\mathbf{B})\tau} = e_{\mathrm{O}_-}^{\int_0^\tau dt\, \exp(\mathbf{A}t)\mathbf{B}\exp(-\mathbf{A}t)} e_{\mathrm{O}_+}^{\int_0^\tau dt\, \exp(\mathbf{A}t)\mathbf{B}\exp(-\mathbf{A}t)}, \quad (3.1)$$

where the symbol O_+ (O_-) stands for the positive (negative) Dyson time ordering. This enables one to transform Eq. (2.7) to

$$g_\pm(2\tau) = \int \mathbf{d}^3\mathbf{r}\, g_\pm(\mathbf{r},2\tau) = \int \mathbf{d}^3\mathbf{r}\, e_{\mathrm{O}_-}^{D_T\int_0^\tau dt\, \exp[\mp i(\chi/2)F(\mathbf{r})t]\nabla^2\exp[\pm i(\chi/2)F(\mathbf{r})t]} \times e_{\mathrm{O}_+}^{D_T\int_0^\tau dt\, \exp[\mp i(\chi/2)F(\mathbf{r})t]\nabla^2\exp[\pm i(\chi/2)F(\mathbf{r})t]} p_{\mathrm{eq}}(\mathbf{r}). \quad (3.2)$$

For the magnetic dipolar potential, one has from Maxwell's equations: $\nabla^2 F(\mathbf{r})=0$. Using the well-known Campbell–Hausdorff expansion,[17] one can expand the operator in the ordered exponentials of Eq. (3.2) in a series of commutators. Fortunately, the third and higher commutators vanish, and one obtains exactly that

$$e_{\mathrm{O}_\pm}^{D_T\int_0^\tau dt\{\nabla^2+(\mp i\chi t/2)[F(\mathbf{r}),\nabla^2]+(1/2)(\mp i\chi t/2)^2[F(\mathbf{r}),[F(\mathbf{r}),\nabla^2]]\}} = e_{\mathrm{O}_\pm}^{D_T\int_0^\tau dt[\nabla^2\pm i\chi t\nabla F(\mathbf{r})\cdot\nabla-(\chi^2t^2/4)|\nabla F(\mathbf{r})|^2]}. \quad (3.3)$$

The squared modulus of the dipolar field gradient is readily found to be

$$|\nabla F(\mathbf{r})|^2 = \frac{5}{16\pi}\left|\nabla\frac{3\cos^2\theta-1}{r^3}\right|^2 = \frac{5}{16\pi}\frac{9}{r^8}(5\cos^4\theta-2\cos^2\theta+1). \quad (3.4)$$

The decay of the electron spin echo due to interactions with the solvent protons that are modulated by the diffusion is then given, from Eq. (2.4), by

$$G(2\tau)=G(0)\exp\left[-C\int \mathbf{d}^3\mathbf{r}\left\{1-\frac{g_+(\mathbf{r},2\tau)+g_-(\mathbf{r},2\tau)}{2}\right\}\times p'_{\mathrm{eq}}(\mathbf{r})\right], \quad (3.5)$$

[where the prime has the same meaning as in Eq. (2.5)]. Equation (3.5) is the exact formal solution to Eqs. (2.4)–(2.6). In the general case it remains a daunting task to solve, and the methods of Refs. 5, 6, 9, and 11, yielding accurate numerical solutions, are more useful. Equation (3.5), however, provides the basis for studying the slow motional limit (i.e., the limit as $D_T\to 0$), especially given its linear dependence upon D_T in the ordered exponent. Useful forms can indeed be obtained from Eq. (3.5) in certain cases. First we note that in the absence of any potential of mean force,[18] one has $p'_{\mathrm{eq}}(\mathbf{r})=1$. Then one finds that the term involving t^2 in the exponential operator of $g(\mathbf{r},2\tau)$, Eq. (3.2) as given by Eq. (3.3), governs both the short- and long-time behavior of Eq. (3.5). That is, at short times τ, one expands the time-ordered exponential in Eq. (3.3) to first order in D_T and only the term in t^2 survives after postmultiplication by $p'_{\mathrm{eq}}(\mathbf{r})=1$, so one obtains

$$G(2\tau)=G(0)\exp\left[-\frac{8\pi}{5}(Cd^3)\left(\frac{D_Td}{\gamma_A\gamma_B\hbar}\right)\left(\frac{\gamma_A\gamma_B\hbar\tau}{d^3}\right)^3\right], \quad (3.6)$$

where d is the distance of minimal approach between the electron spin and the protons.

For long τ, the t^2 term in Eq. (3.3) clearly dominates, so we drop the other two terms. The resulting integral in the exponent leads to an incomplete gamma function which may be evaluated asymptotically[19] in the limit of large τ (or more rigorously $D_T\chi^2\tau^3d^{-8}\to\infty$) to yield

$$G(2\tau)=G(0)\exp\left\{-\frac{4\pi}{3}(Cd^3)\left[I\Gamma\left(\frac{5}{8}\right)\times\left(\frac{3D_Td}{2\gamma_A\gamma_B\hbar}\right)^{3/8}\left(\frac{\gamma_A\gamma_B\hbar\tau}{d^3}\right)^{9/8}-1\right]\right\}. \quad (3.7)$$

Note that in Eqs. (3.6) and (3.7) all quantities in the parentheses are combined to form dimensionless factors. In deriving Eq. (3.7) we have used the following integrals: $\int_0^{1/d^8}(1-e^{-\alpha x})x^{-11/8}dx\approx\frac{8}{3}[\alpha^{3/8}\Gamma(\frac{5}{8})-d^3]$ valid for $d\to 0$ and $I\equiv\int_0^1(5x^4-2x^2+1)^{3/8}dx\approx 1.081$. To obtain the first integral, we have expanded the incomplete Gamma function up to the first order[19] to ensure proper dimensional regularization of all parameters in Eq. (3.7) when $d\to 0$. Note that since the dipolar-field gradient, $|\nabla F(\mathbf{r})|$, is just an ordinary function of **r**, the Dyson time ordering can be omitted in evaluating Eq. (3.5) for the above limiting cases.

IV. COMPARISON WITH NUMERICAL SOLUTIONS AND DISCUSSION

As can be seen from the superexponential character of Eq. (3.5), when concentrations are high, i.e., $Cd^3\gg 1$, so the echo decay is relatively rapid, then the short-time behavior on the two-body time scale governs many-body relaxation, i.e., Eq. (3.6) will be appropriate. At lower concentrations the phase memory of a many-spin system is described by a more complicated function, involving both Eqs. (3.6) and (3.7), as we show below.

The short-time τ^3 behavior exhibited by Eq. (3.6) is to be expected. It represents the well-known short-time result for ''single-body'' relaxation for such cases as spin dephasing due to translational diffusion in a field-gradient in the Carr–Purcell pulse sequence[20] and for modulation of an an-

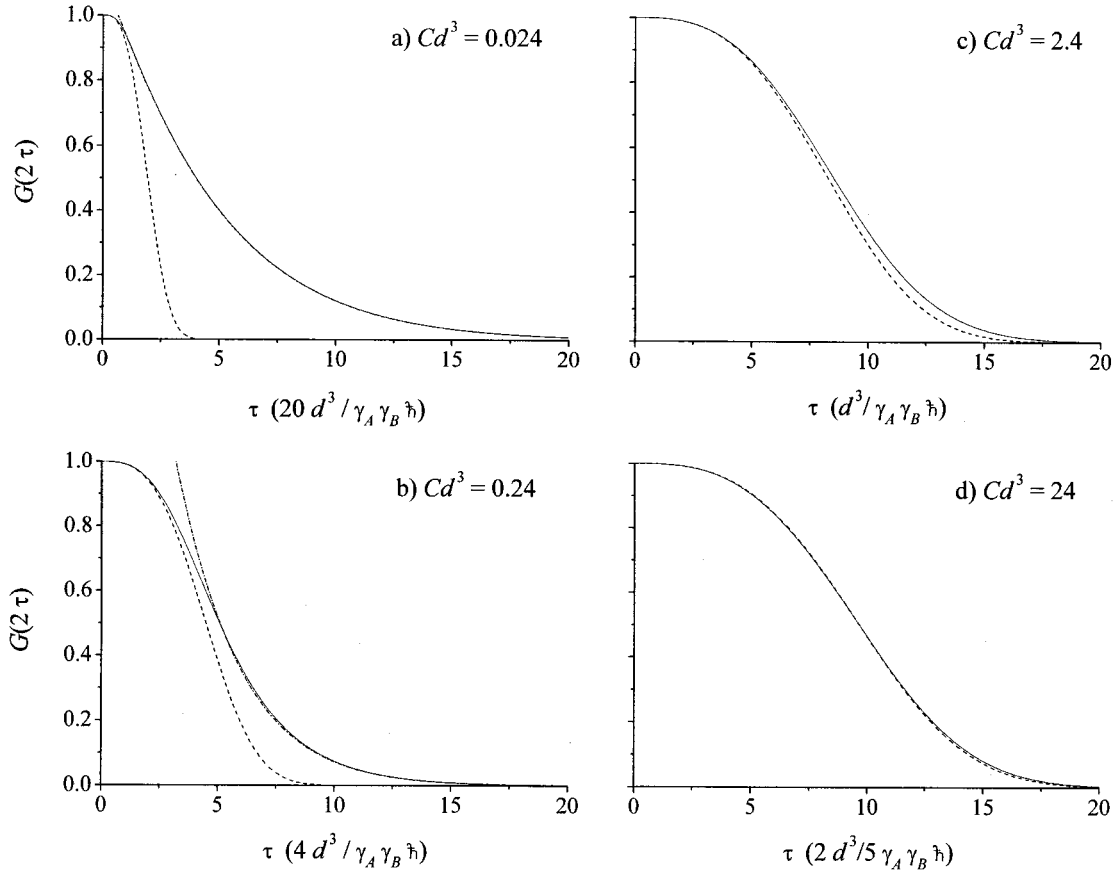

FIG. 1. Electron spin-echo envelopes as a function of pulse delay time at different proton concentrations in the slow motional regime, $D_T = 10^{-4}\gamma_A\gamma_B\hbar/d$. The short-time expression, Eq. (3.6), and long-time expression, Eq. (3.7), are represented by dashed and dot-dashed lines, respectively; the solid lines are the exact numerical results obtained from Eq. (2.3).

isotropic spin Hamiltonian by molecular rotational diffusion.[10] The fact that the two-body expression is exponentiated in Eq. (3.5) will lead to Eq. (3.6) being valid over a longer time-scale than the two-body result, as seen in the comparison with the exact results below.

The long-time $\tau^{9/8}$ exponential behavior of Eq. (3.7) for slow motion is modified from the well-known exponential behavior in τ/T_2 in the motional-narrowing regime, as is the power law dependence on D_T.

Plots of the echo envelopes are shown in Fig. 1 for $D_T = 10^{-4}\gamma_A\gamma_B\hbar/d$, corresponding to the nearly rigid limit. Case (a) corresponds to low concentrations, with intermediate concentrations (b), and high concentrations (c and d). Solid lines show the results of numerical solution of Eq. (2.3) by using the SLE, Eq. (2.6), cf. Refs. 5 and 9, and the dashed lines correspond to the limiting behavior given by Eqs. (3.6) and (3.7). If the distance of minimal approach is set to $d = 3$ Å, (a) corresponds to rather dilute solutions with proton concentrations, C of 8.9×10^{20} cm^{-3}; (b) is for $C = 8.9\times10^{21}$ cm^{-3}; and (c) corresponds to a C (8.9×10^{22} cm^{-3}) similar to pure water (6.6×10^{22} cm^{-3}).[21] Case (d) is for unphysically high concentrations of 8.9×10^{23} cm^{-3} to show the limiting cubic behavior of the echo envelope decay. Case (a) is dominated by the long time $\tau^{9/8}$ behavior, but with τ^3 behavior at very early times. Case (b) shows an increased (decreased) role for the latter (former).

Figure 2 shows the echo envelopes calculated for different diffusion rates D_T, for $Cd^3 = 0.24$. As in Fig. 1, solid lines designate the numerical solutions. Equations (3.6) and (3.7) are seen to be useful asymptotic expressions for the echo envelopes over the slow motional range, i.e., for $D_T \leqslant 10^{-3}\gamma_A\gamma_B\hbar/d$. But the validity of Eqs. (3.6) and (3.7) breaks down at sufficiently fast motions, i.e., for $D_T \geqslant 10^{-2}\gamma_A\gamma_B\hbar/d$. (These dimensionless inequalities become $D_T \leqslant 10^{-11}$ cm^2/s and $D_T \geqslant 10^{-10}$ cm^2/s, respectively using a $d = 3$ Å and the appropriate gyromagnetic ratios.) That is, Eq. (3.6) is applicable only for much shorter times as D_T increases. Equation (3.7) becomes inapplicable as D_T increases, most likely as a result of the terms in t^0 and t^1 in the exponent of Eq. (3.3) becoming more important during intermediate time periods [recall that these terms in Eq. (3.3) require integration over t].

These comparisons thus demonstrate the essential validity of the asymptotic forms in the very slow motional regime. In addition, they show that the echo envelope decay cannot be expressed by a simple exponential even at longer delay times. This explains an apparent anomaly previously seen in analyzing the numerical results for the concentration dependence of the echo decay. This was performed using a simple

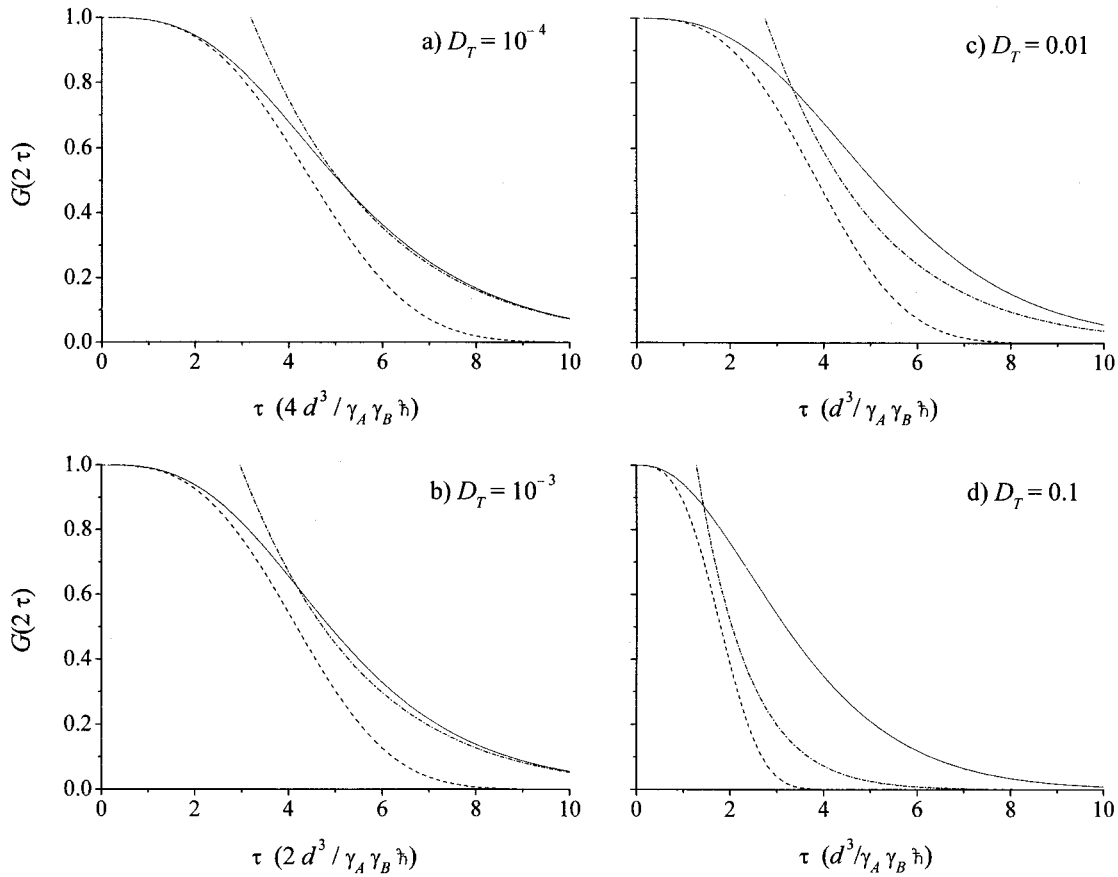

FIG. 2. Electron spin-echo envelopes as a function of pulse delay time at different translational diffusion rates, D_T, as shown. The proton concentration is set to $Cd^3 = 0.24$ (intermediate concentration regime) to capture both the short- and long-time limiting behavior, cf. Eqs. (3.6) and (3.7). (The different lines are as in Fig. 1).

exponential in time and results in a C^a with[5] $a \approx 0.9$ which is close to $\frac{8}{9}$. This is equivalent to linear dependence on C when the proper $\tau^{9/8}$ power is used. Note also that the $D_T^{3/8}$ power law dependence on the diffusion coefficient would become an effective $D_T^{1/3}$ power law from fitting the echo envelopes to a simple exponential decay function (instead of $\tau^{9/8}$), and this is in agreement with the 0.34 ± 0.02 power law obtained numerically.[5,9]

The closed-form solutions derived herein break down when motions become sufficiently fast, i.e., when the line broadening is essentially homogeneous.[5] In this limit the well-known Torrey–Redfield theory is appropriate [e.g., the spectral density $J(0)$ that contributes to the transverse spin relaxation is given by $J(0) \propto (4/15)(C/d\,D_T)$]. In the ultraslow motional regime considered herein, the asymptotic equations for the transverse spin relaxation, while more complex, can still be written in terms of the coefficient for relative diffusion, D_T, the distance of closest approach, d, and the concentration, C. This result could potentially be of use to aid in studying ultraslow motional relaxation in polymers, glasses, and semi-ordered media. One caveat, however, is that in the rigid limit, relaxation due to translational diffusion is no longer relevant, and the phase memory decay for the electron-spin is dominated by effects of nuclear spin diffusion, which, however are readily averaged out by motion.[9]

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APPENDIX: DERIVATION OF EQ. 3.1

To derive Eq. (3.1) we note that the time evolution of an arbitrary function $\mathbf{g}(\tau)$ obeying the equation

$$\frac{\partial \mathbf{g}(\tau)}{\partial \tau} = (\mathbf{A}+\mathbf{B})\mathbf{g}(\tau) \tag{A1}$$

is given by $\mathbf{g}(\tau) = \exp[(\mathbf{A}+\mathbf{B})\tau]\mathbf{g}(0)$. By substituting $\mathbf{g}(\tau) = \exp(\mathbf{A}\tau)\hat{\mathbf{g}}(\tau)$ into Eq. (A1) and integrating we find that

$$e^{(\mathbf{A}+\mathbf{B})\tau} = e^{\mathbf{A}\tau} e_{\mathrm{O}_+}^{\int_0^\tau dt\, \exp(-\mathbf{A}t)\mathbf{B}\exp(\mathbf{A}t)}. \tag{A2}$$

Or, by taking the transpose of both sides of Eq. (A2),

$$e^{(\mathbf{A}+\mathbf{B})\tau} = e_{\mathrm{O}_-}^{\int_0^\tau dt\, \exp(\mathbf{A}t)\mathbf{B}\exp(-\mathbf{A}t)} e^{\mathbf{A}\tau} \tag{A3}$$

since $\mathbf{A}$ and $\mathbf{B}$ are symmetric. If we replace $\mathbf{A}$ by $-\mathbf{A}$ in Eq. (A2) and multiply it by Eq. (A3) from the left we get Eq. (3.1).

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[21] Note that our analysis neglects the correlated relaxation effects of the pair of protons on each water molecule.