Low-Temperature Quantum Relaxation in a System of Magnetic Nanomolecules

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We argue that to explain recent resonant tunneling experiments on crystals of Mn_{12} and Fe_8, particularly in the low-T limit, one must invoke *dynamic* nuclear spin and dipolar interactions. The low-T, short-time relaxation will then have a $\sqrt{t/\tau}$ form, where τ depends on the nuclear T_2, on the tunneling matrix element Δ_{10} between the two lowest levels, and on the initial distribution $N(\xi)$ of internal fields in the sample, which depends strongly on sample shape. We also give results for the long-time relaxation. [S0031-9007(98)06470-9]

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Recent experiments on magnetic relaxation of molecular crystals of Mn_{12} and Fe_8 find strong evidence for tunneling-mediated relaxation at low T [1–7]. This evidence comes from resonances observed in the relaxation rate at certain values of external magnetic field H (when energy levels of magnetic states on opposite sides of the potential barrier match each other). The resonances exist in the low-T limit (when only the two lowest electronic energy levels of each molecule are involved), and also in the thermally activated regime, when tunneling takes place between higher levels. Their linewidth is roughly 0.1 T (for Mn_{12}) or 0.05 T (for Fe_8). In the Fe_8 system, the low-T relaxation rate peak near $H = 0$ is 10^4 times the rate at $H = 0.1$ T, off resonance.

The anisotropic potential acting on these molecular "giant spins" (spin quantum number S) is dominated by a strong easy-axis term ${}^{\parallel}\mathcal{H}_2^{(0)} = -(\mathcal{D}/S)S_z^2$; tunneling is caused by weak transverse perturbations. For Fe_8, $\mathcal{D} \sim 2.7$ K, whereas in Mn_{12}, $\mathcal{D} \sim 6.1$ K; and $S = 10$ for both [1–7]. Here we concentrate on the low-T relaxation (below $T_c \sim 2.2$ K and $\sim$0.4 K, for Mn_{12} and Fe_8, respectively [8]), near $H = 0$, so that only the two levels $|10\rangle$ and $|-10\rangle$ of ${}^{\parallel}\mathcal{H}_2^{(0)}$ are involved—they are coupled by a tunneling matrix element Δ_{10}, which can in principle be calculated [9], but only if all relevant transverse couplings are known [10]. Present estimates range over several orders of magnitude, but it seems unlikely that Δ_{10} exceeds 10^{-8} K for either system—here we treat it as an independent parameter.

The low-T, low-H limit is particularly interesting because of the following simple reasoning. Recall first that standard phase space arguments [11] tell us that the phonon-mediated spin relaxation goes like $\tau^{-1} \sim \xi^3[2\mathcal{N}(\xi) + 1]$, where $\xi = |\mathcal{E}_S - \mathcal{E}_{-S}|$ is the bias between the two lowest levels, and $\mathcal{N}(\xi)$ is the Bose function. If we ignore hyperfine, dipolar, and Dzyaloshinskii-Moriya fields, $\xi = 2g\mu_B S|H|$, and we get $\tau^{-1} \sim |H|^3$; however, even these fields will not change the prediction of a minimum in τ^{-1} around $H = 0$, *unless* we include their *dynamics*. This is because the typical bias caused by dipolar fields alone is $\xi_{\mathrm{dip}} \sim 0.1$–$0.5$ K; with Δ_{10} in the nanokelvin range, a distribution of *static* hyperfine and dipolar fields in the sample will simply force almost all molecules off resonance (resonant tunneling requiring that $\xi < \Delta_{10}$, in the low-T limit). The only way for the molecules to relax is then via spin-phonon interactions, and spread in static fields simply smears the minimum around $H = 0$. Moreover, for $T < T_c$ and static bias $\xi \sim \xi_{\mathrm{dip}}$, the phonon-mediated relaxation is astronomically long.

This argument holds even if the static fields have a transverse component, unless this is $\sim$3–5 T (enough to raise Δ_{10} to the experimental resonance linewidth, i.e., $\sim$0.1–1 K for the Mn_{12} and Fe_8 systems [12]); this is $\sim 10^2$ times the actual hyperfine/dipolar field combination. Thus the low-field, low-T experiments force us to consider the *dynamics* of the hyperfine and dipolar fields, which, by varying the bias at each molecular site in time, can continually bring more molecules to resonance [13].

At first glance, in the low-T limit only the dynamic nuclear fields (i.e., hyperfine and nuclear dipolar fields) can then cause relaxation—once $kT \ll \mathcal{D}$, all dipolar flip-flop processes are frozen out [14]. However, we shall see that although we need the rapidly fluctuating hyperfine field to bring molecules initially to resonance, the ensuing gradual adjustment of the dipolar fields across the sample, caused by tunneling relaxation, brings a steady supply of molecules further into resonance, and allows continuous relaxation. This process is particularly important in Fe_8, where hyperfine couplings are small. The fluctuating nuclear spin field also makes the tunneling *incoherent*. One can then write a classical kinetic equation for the magnetization, whose solution at short time is found below to have a square root behavior, for almost any sample shape (although the characteristic decay time depends strongly on the shape).

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We thus find that not only do the low-T, low-H experimental results force the internal field *dynamics* into the theory—this dynamics also leads to an experimentally testable prediction for the form of the relaxation.

We will treat the problem using a Hamiltonian

$$H = \frac{1}{2}\sum_{ij} V_{ij}^{(d)} \tau_z^{(i)} \tau_z^{(j)} + \sum_i \Delta_{10} \tau_x^{(i)} + \sum_{ik} V^{(N)}(\tau_z^{(i)}, \vec{I}_k) + H^{NN}, \tag{1}$$

where the first term describes the dipolar-dipolar interactions between molecules, the second describes tunneling, the third couples magnetic molecules to nuclear spins $\{\vec{I}_k\}$, and the last term describes interactions between the nuclear spins. This is an effective Hamiltonian operating in the subspace of the two lowest levels of each molecule; we choose the basis set to be $|S_z = \pm S\rangle$; τ_z and τ_x are Pauli matrices, and $\{i\}$, $\{j\}$ label molecular sites.

We have ignored the transverse part of the dipolar coupling, since it only renormalizes Δ_{10} in an unmeasurable way—all flip-flop transitions to states with $S_z \neq \pm S$ are frozen out at low T. Nuclear spin effects are more subtle—however, since the dipolar fields in (1) are diagonal and static unless molecules flip, one need understand only the dynamics of individual molecules, coupled to the nuclear bath, assuming that dipolar fields are frozen. This problem was solved in Ref. [15], Sec. 4. If the nuclear T_1 is long (which it will be at these temperatures, since it is driven by dipolar flip-flop processes), then the hyperfine bias field on a given molecule rapidly fluctuates at a rate T_2^{-1}, over an energy scale Γ_2 which is also roughly $\sim T_2^{-1}$. Typically $T_2^{-1} \sim 10^{-7}$–10^{-5} K, so we expect $\Delta_{10} \ll T_2^{-1}$. Thus at short times we write the bias $\xi_j(t)$, at molecular site j, as $\xi_j(t) = \xi_j + \delta\xi_j(t)$, where ξ_j results from the sum of the quasistatic dipolar and hyperfine fields, with only a small rapidly fluctuating component $\delta\xi_j(t)$, which nevertheless sweeps over a bias range much larger than Δ_{10}. One then finds [15] that a molecule in quasistatic bias ξ relaxes *incoherently* at a rate

$$\tau_N^{-1}(\xi) \approx \tau_0^{-1} e^{-|\xi|/\xi_o}. \tag{2}$$

$$\tau_N^{-1}(\xi = 0) \equiv \tau_0^{-1} \approx \frac{2\Delta_{10}^2}{\pi^{1/2}\Gamma_2}. \tag{3}$$

The parameter ξ_0 depends on the average number λ of nuclear spins coflipping with S. If $\lambda < 1$, then $\xi_0 \sim \Gamma_2$; for $\lambda \gg 1$, $\xi_0 \sim \lambda |V_{ki}^{(N)}|$. For Fe$_8$ and Mn$_{12}$, $\lambda < 1$ is likely [16]; in any case, $\xi_0 \ll E_D$, where E_D is the total dipolar coupling from nearest neighbor molecules, and the exact value of ξ_0 is not too important.

We now define a normalized one-molecule distribution function $P_\alpha(\xi, \vec{r}; t)$, with $\sum_\alpha \int d\xi \int d\vec{r}\, P_\alpha(\xi, \vec{r}; t) = 1$. It gives the probability of finding a molecule at position $\vec{r}$, with polarization $\alpha = \pm 1$ (i.e., in state $|S_z = \pm S\rangle$), having a bias energy ξ, at time t. Molecules having bias energy ξ undergo transitions between $|S_z = S\rangle$ and $|S_z = -S\rangle$ at a rate given by (2).

To derive a kinetic equation for $P_\alpha(\xi, \vec{r}; t)$, we again assume dipolar and hyperfine fields are frozen (apart from the T_2 fluctuations just discussed), *unless* a molecule flips. All kinetics then comes from these flips, along with the resulting adjustment of the dipolar field. We then derive a kinetic equation in the usual way, by considering the change in P_α in a time δt, caused by molecular flips, at the rate $\tau_N^{-1}(\xi)$, around the sample. This yields

$$\dot{P}_\alpha(\xi, \vec{r}) = -\tau_N^{-1}(\xi)[P_\alpha(\xi, \vec{r}) - P_{-\alpha}(\xi, \vec{r})] - \sum_{\alpha'} \int \frac{d\vec{r}\,'}{\Omega_0} \int \frac{d\xi'}{\tau_N(\xi')} \times [P_{\alpha\alpha'}^{(2)}(\xi, \xi'; \vec{r}, \vec{r}\,') - P_{\alpha\alpha'}^{(2)}(\xi - \alpha\alpha' V_D(\vec{r} - \vec{r}\,'), \xi'; \vec{r}, \vec{r}\,')], \tag{4}$$

where $P_{\alpha\alpha'}^{(2)}(\xi, \xi'; \vec{r}, \vec{r}\,'; t)$ is the two-molecule distribution, giving the normalized joint probability to find a molecule at site $\vec{r}$, in state $|\alpha\rangle$ and bias ξ, while another is at $\vec{r}\,'$, in state $|\alpha'\rangle$, and bias ξ'. $P^{(2)}$ is linked to higher multimolecule distributions by a Bogoliubov-Born-Green-Kirkwood-Yvon (BBGKY)-like hierarchy of equations. The first term on the right-hand side of (4) describes the local tunneling relaxation; the second nonlocal term (analogous to a collision integral) comes from the change in the dipolar field at $\vec{r}$, caused by a molecular flip at $\vec{r}\,'$; the dipolar interaction $V_D(\vec{r}) = E_D[1 - 3\cos^2\theta]\Omega_0/r^3$, where Ω_0 is the unit molecular cell volume, and $\int d\vec{r}\,'$ integrates over the sample volume.

We assume that at $t = 0$ the sample is fully polarized; the initial relaxation is then treated in a dilute solution approximation for the fraction $(1 - M)/2 \ll 1$ of flipped molecules (where $M = \int d\xi \int (d\vec{r}/\Omega_0)[P_+(\xi, \vec{r}) - P_-(\xi, \vec{r})] \equiv \int d\xi \int (d\vec{r}/\Omega_0) M(\xi, \vec{r})$). The bimolecular distribution function $P^{(2)}$ factorizes in this limit [17], i.e., $P^{(2)}(1,2) = P(1)P(2)$. We begin with a field-compensated *ellipsoidal* sample, with uniform demagnetization field. The field distribution around randomly placed dipoles is a Lorentzian [18] up to a high-energy cutoff E_D:

$$P_\alpha(\xi) = \frac{1 + \alpha M(t)}{2} \frac{\Gamma_d(t)/\pi}{[\xi - \alpha E(t)]^2 + \Gamma_d^2(t)};$$

$$\Gamma_d(t) = \frac{4\pi^2}{3^{5/2}} E_D[1 - M(t)]; \tag{5}$$

$$E(t) = cE_D[1 - M(t)], \tag{6}$$

where c is a sample shape dependent coefficient [19], and $E(t)$ is the time dependent internal field. Then (4) gives

$$\dot{M}(t) = -M(t)\frac{2}{\tau_0}\int d\xi\, e^{-|\xi|/\xi_0}\frac{\Gamma_d(t)/\pi}{[\xi - E(t)]^2 + \Gamma_d^2(t)}\,. \tag{7}$$

At very short times $t < \tau_0\xi_0/E_D$ this gives a linear relaxation $M(t) = 1 - 2t/\tau_0$, unobservable because $\xi_0/E_D \ll 1$. For $t \gg \tau_0\xi_0/E_D$ one gets

$$\dot{M}(t) = -\frac{1}{2\tau_{\text{short}}}\frac{M(t)}{1 - M(t)}\,; \tag{8}$$

$$\tau_{\text{short}}^{-1} = \frac{\xi_0}{E_D\tau_0}\frac{32\pi}{3^{5/2}(c^2 + 16\pi^2/3^5)}\,. \tag{9}$$

Since (7) itself is only valid when $1 - M(t) \ll 1$, we simply write

$$M(t) \approx 1 - \sqrt{t/\tau_{\text{short}}}\,; \qquad \left(\frac{E_D}{\xi_0} > \frac{t}{\tau_0} > \frac{\xi_0}{E_D}\right). \tag{10}$$

This square-root behavior should be observable over a wide time range, since $E_D/\xi_0 \gg 1$. Note also that τ_{short} is sample shape dependent even for a *homogeneous* demagnetization field. If the sample is not ellipsoidal, then the above analysis is incorrect—the problem becomes essentially inhomogeneous. We then return to the kinetic Eq. (4)—if the demagnetization varies on a length scale much greater than the average distance between flipped spins, then (7) is modified to

$$\dot{M}(\vec{r},t) = -M(\vec{r},t)\frac{2}{\tau_0}\int\frac{d\xi}{\pi} \times \frac{\Gamma_d(\vec{r},t)e^{-|\xi|/\xi_0}}{[\xi - E(\vec{r},t)]^2 + \Gamma_d^2(\vec{r},t)}\,, \tag{11}$$

where $\Gamma_d(\vec{r},t)$ and $E(\vec{r},t)$ are defined in terms of $M(\vec{r},t)$ analogously to (5) and (6); the solution is then identical to (10) except that τ_{short} is modified to

$$(\tau_{\text{short}}^{(\text{inh})})^{-1} \sim \xi_0 N(0)\tau_{\text{short}}^{-1}\,, \tag{12}$$

where $N(0) = \int d\vec{r}\,\sum_\alpha P_\alpha(\xi = 0, \vec{r}; t = 0)$ is the *initial* "density of states" for the dipolar field distribution, integrated over the whole sample, at bias $\xi = 0$; typically $N(0) \sim 1/E_{Dm}$, where E_{Dm} is the average demagnetization field.

To verify these results, and see when the square-root behavior breaks down, we performed Monte Carlo (MC) simulations of the relaxation for various sample geometries. During each time interval $\delta t \ll \tau_0$ one flips molecules with probability $1 - \exp\{-\delta t/\tau_N(\xi)\}$ and then recalculates the dipolar field distribution, now altered by the flipped molecules (cf. Fig. 1). The system size we can simulate is not really macroscopic [20], but finite size corrections do not change the two main predictions of Eqs. (9)–(12), viz., (i) universality of the square-root relaxation at short times and (ii) the characteristic dependence of (12) on the sample geometry. Clearly, the fastest relaxation will be in nearly ellipsoidal samples.

Our calculations are most immediately applicable to the Fe_8 system [7], where the field distribution is almost entirely due to dipolar spread [21]. Confirmation of our predictions would then provide strong evidence for the dynamic relaxation mechanism discussed here. We emphasize that at higher T we do *not* expect $\sqrt{t}$ relaxation, since then dipolar flip-flop processes interfere, T_1 becomes short [22], and the magnetization reversal proceeds via higher levels, through mixed activation/tunneling processes. Coupling to the phonon bath is then crucial, which essentially changes the theory.

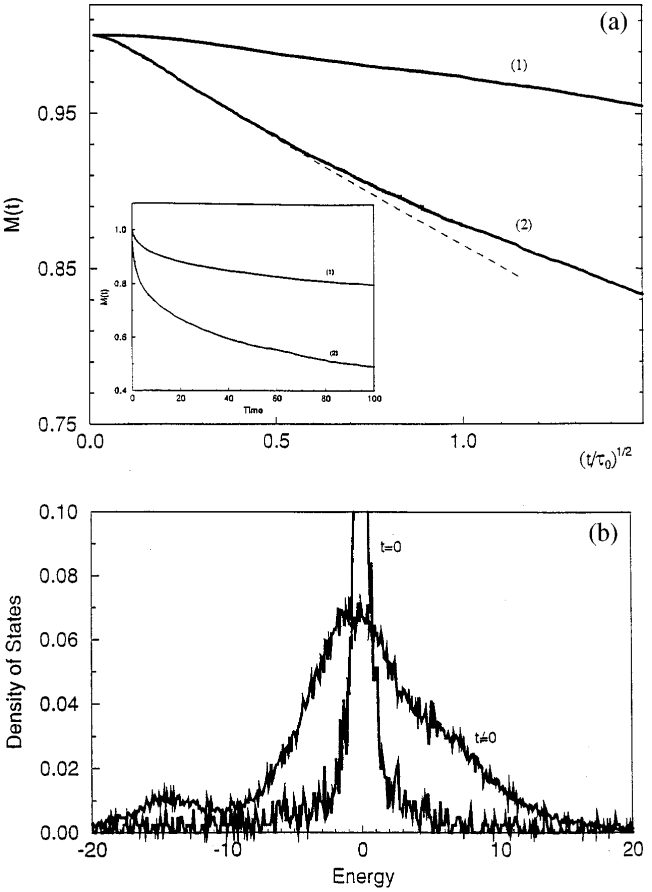

FIG. 1. Monte Carlo simulations of the relaxation in two samples made from a cubic lattice of molecules. In (a) $M(t)$ is shown as a function of $\sqrt{t/\tau_0}$ for (1) a cubic sample of $(50)^3$ molecules, and (2) for a sphere of diameter 50 lattice spacings [the inset shows $M(t)$ as a function of t/τ_0]. The dashed line shows $\sqrt{t}$ behavior; we see multimolecule correlation effects once $M(t) \lesssim 0.93$. In (b) the density of states $N(\xi)$ for the bias field, integrated over the spherical sample (cf. text), is shown at $t = 0$ (where finite size effects smear the zero energy delta function), and $t = 0.1\tau_0$. The latter is distorted at high bias by nearest neighbor lattice effects. We use units where $\xi_0 = 1$ and $E_D = 20$. The fraction of states in the resonant window of width ξ_0 around zero energy, at $t = 0$, was 0.79 (sphere), and 0.037 (cube); the ratio $\sqrt{0.79/0.036} \approx 4.6$ is close to the ratio $\sim$4 between the straight-line slopes in (a).

Another test of our theory is provided by the field dependence near $H = 0$ of $\tau_{\text{short}}^{(\text{inh})}$. According to Eq. (12) this is proportional to $N(\xi = g\mu_B SH)$, the density of states at a bias shifted by the external field, which thus "scans" across the spectrum of bias energies in the inhomogeneous magnet. $N(\xi)$ can be calculated numerically for a given sample shape [23], and then compared directly with the measured dependence of $\tau_{\text{short}}^{(\text{inh})}$ on H. The experimental line shape (and position) are thus also *sample dependent*.

Finally, we consider the relaxation when $t \gg \tau_{\text{short}}$. This problem is greatly complicated by the development of intermolecular correlations in $P^{(2)}$, $P^{(3)}$, etc. However, one way of avoiding this *experimentally* would be to let the system substantially relax at high T, then cool to low T; one is then in the long-time relaxation regime, but with initial condition arranged to give a factorizable $P^{(2)}$. Another analytic solution for the homogeneous (i.e., ellipsoidal) case can then be found from (4), when $M \ll 1$ and $P_{\alpha\alpha'}^{(2)}(\xi, \xi'; \vec{r}, \vec{r}') = P_{\alpha}(\xi) P_{\alpha'}(\xi')$; one finds *exponential* relaxation, at a rate

$$\tau_{\text{long}}^{-1} \approx \frac{2\xi_0}{E_{\max}\tau_0[1 + \kappa \ln(E_{\max}/\pi\xi_0)]}, \qquad (13)$$

where $\kappa \sim 1$ is a numerical coefficient, and $E_{\max}$ is the spread in dipolar fields in this nearly depolarized limit. Details of the derivation will be given elsewhere.

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[8] These numbers are from the experiments [5,7]; the relaxation rate is T independent below T_c.

[9] See, e.g., L. van Hemmen and A. Suto, Physica (Amsterdam) **141B**, 37 (1986); M. Enz and R. Schilling, J. Phys. C **19**, 1765 (1986), and references therein.

[10] Even very small higher-order transverse couplings (up to the 20th order in S^+ and S^-) can make important contributions to Δ_{10}, because lower-order couplings contribute to Δ_{10} with large exponents [e.g., the coupling ${}^{\perp}\mathcal{H}_0^{(2)} = E(S_x^2 - S_y^2)$ gives a contribution $\sim E(E/2\mathcal{D})^9$]. This makes Δ_{10} impossible to calculate, since such higher-order couplings are unmeasurable.

[11] A. Abragam and A. Bleaney, *Electron Paramagnetic Resonance of Transition Ions* (Clarendon, Oxford, 1970); P. Politi *et al.,* Phys. Rev. Lett. **75**, 537 (1995). The latter work predicted a minimum in the relaxation rate at $H = 0$, whereas a maximum is seen; cf. A. L. Burin *et al.,* Phys. Rev. Lett. **76**, 3040 (1996), and Politi *et al.,* *ibid.* **76**, 3041 (1996).

[12] Recall that the contribution to Δ_{10} from a static transverse H is $\sim g\mu_B S H_{\perp}(g\mu_B S H_{\perp}/\mathcal{D})^{19}$; for Mn_{12} and Fe_8, $(\mathcal{D}/g\mu_B S) \sim 10$ and ~ 5 T, respectively.

[13] For the effect of dynamic external (c-number) fields, see, e.g., L. Gunther, Europhys. Lett. **39**, 1 (1997).

[14] The dipolar flip-flop transitions at low T go at rate $\lambda_{fl} \sim \Omega_{\text{dip}} \exp\{-(\mathcal{E}_9 - \mathcal{E}_{10})/k_B T\}$, where $\Omega_{\text{dip}} \sim 10^6$–$10^8$ Hz. The *direct* effect of these processes is small [the concentration of molecules in $|9\rangle$ is $\sim\exp\{-(\mathcal{E}_9 - \mathcal{E}_{10})/k_B T\}$]; they are dangerous only because they drive nuclear T_1 processes, which sweep ξ over a much larger range than ξ_0. If the hyperfine coupling is strong enough, terms $\sim\lambda\Omega_{\text{dip}} S_i^+ S_j^- I_i^- I_j^+$ can also drive T_2 processes (giving an activated T dependence to T_2).

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[16] If all nuclear spin effects come from the hyperfine coupling, $\lambda \sim \sum_k (\omega_k/\mathcal{D})^2 \ll 1$ (cf. Ref. [15]), for both the Mn_{12} and Fe_8 systems. Nuclear dipole-dipole interactions change this estimate, but not drastically.

[17] When $x = 1 - M$ is small, then (i) dynamical corrections coming from cooperative multiflip processes are very small (of order $\sim\Delta_{10}^4/\xi_o^2 E_D$), and (ii) static field corrections distorting our Lorentzian ansatz are $\sim x^2$; our Monte Carlo results show these are insignificant until $x \sim 0.15$.

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[19] The coefficient c is defined by Eq. (6). For a prolate spheroid, $c = (2\pi/3)[a^4 + a^2 - 3a\sqrt{a^2 - 1} \ln(a + \sqrt{a^2 - 1}) - 2]/(a^2 - 1)^2$, where a is the ratio of the longitudinal axis to its perpendicular; analytic formulas can be found for any ellipsoid.

[20] Even with 10^5 molecules, statistical fluctuations in $P_\alpha(\xi, t)$ inside the small resonance window (width ξ_0) are large unless $E_D/\xi_0 \gtrsim 30$ [which correspondingly limits the time scale over which (10) is observed]. In real systems E_D/ξ_0 can be very large.

[21] In Fe_8, the hyperfine field is ~ 3 G (due mainly to protons); in Mn_{12}, it is more like 250 G. In both systems, $E_D \sim 1000$ G. Provided $T_1 \gg \tau_{\text{short}}$ (so only T_2 fluctuations matter), the $\sqrt{t}$ prediction holds; however, the large random hyperfine field in Mn_{12} means that (12) is no longer precisely obeyed.

[22] When $T_1 \ll$ the experimental time scale *and* hyperfine fields are comparable to or larger than intermolecular dipolar fields, one gets exponential relaxation [15].

[23] For many systems the fastest relaxation will not occur at $H = 0$, even for spheres, because Dzyaloshinskii-Moriya interactions cause an extra static uniform bias.