

NMR as a Probe of the Relaxation of the Magnetization in Magnetic Molecules

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We investigate the time autocorrelation of the molecular magnetization $M(t)$ for three classes of magnetic molecules (antiferromagnetic rings, grids, and nanomagnets), in contact with the phonon heat bath. For all three classes, we find that the exponential decay of the fluctuations of $M(t)$ is characterized by a single characteristic time $\tau(T, B)$ for not too high temperature T and field B . This is reflected in a nearly single-Lorentzian shape of the spectral density of the fluctuations. We show that such fluctuations are effectively probed by NMR, and that our theory explains the recent phenomenological observation by Baek *et al.* [Phys. Rev. B **70**, 134434 (2004)] that the Larmor-frequency dependence of $1/T_1$ data in a large number of AFM rings fits to a single-Lorentzian form.

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A central aspect of the physics of magnetic molecules is the way molecular observables, and particularly the magnetization M , are affected by interactions of the spins with other degrees of freedom. When the latter behave as a heat bath, they cause decoherence of the time evolution of molecular observables, usually leading to relaxation dynamics and exponential time decay of equilibrium fluctuations. The understanding and characterization of relaxation mechanisms in crystals containing magnetic molecules is not only important for evident fundamental reasons, but also because relaxation and, more generally, decoherence constitute a major obstacle in the envisaged technological applications of these molecules as classical [1] or quantum [2] bits. In this Letter, we show that for three important classes of magnetic molecules [antiferromagnetic (AFM) rings, grids, and nanomagnets], the exponential decay of the fluctuations of $M(t)$ due to spin-phonon interactions is dominated by a *single* characteristic time $\tau(T, B)$ over a wide range of temperatures and applied fields. While this was already known for the long-time decay of M in nanomagnets, our results show that this applies to completely different classes of molecules, and holds on much shorter time scales as well. Indeed, in the considered (T, B) regimes this single characteristic frequency $\lambda_0 = 1/\tau$ dominates the fluctuations spectrum to such a large extent that even experimental probes whose intrinsic frequency is very different from λ_0 will nevertheless detect mostly this single spectral contribution. In particular, we show that NMR measurements of the longitudinal nuclear relaxation rate $1/T_1$ can be used as a direct probe of the fluctuations of M , and that experimental $1/T_1$ data are fully consistent with our picture. For instance, we explain the recent experimental observation [3] that the Larmor-frequency dependence of $1/T_1$ data in a large number of AFM rings fits to a Lorentzian form, and we elucidate the meaning and behavior of the characteristic time $\tau(T, B)$ of this Lorentzian. In addition, we collected new data on the Mn 3×3 grid which give further support to our picture. At last, we reanalyzed NMR data on the prototype nanomagnet Fe₈.

Each magnetic molecule can be described by the spin Hamiltonian

$$H = \sum_{i>j=1,N} J_{ij} \mathbf{s}_i \cdot \mathbf{s}_j + \sum_{i=1,N} \sum_{k,q} b_k^q(i) O_k^q(\mathbf{s}_i) + \sum_{i>j=1,N} \mathbf{s}_i \cdot \mathbf{D}_{ij} \cdot \mathbf{s}_j - g\mu_B \mathbf{B} S_z, \quad (1)$$

where \mathbf{s}_i are spin operators of the i th magnetic ion in the molecule. The first term is the isotropic Heisenberg exchange interaction. The second term describes local crystal fields (CFs), with $O_k^q(\mathbf{s}_i)$ Stevens operator equivalents for the i th ion [4] and $b_k^q(i)$ CF parameters. The third term represents dipolar anisotropic intracluster spin-spin interactions. The last term is the Zeeman coupling with an external field \mathbf{B} with $S_z = \sum_i s_{i,z}$. The Heisenberg contribution is usually largely dominant, and therefore the energy spectrum of H consists of a series of level multiplets with an almost definite value of the total spin S . Much of the physics of nanomagnets such as Fe₈ can be described to a good degree of approximation by retaining the lowest S multiplet [5]. In AFM rings such as Fe₆ and Cr₈ and in grids, several distinct S multiplets must be included for a good description. The ground and first-excited multiplets have $S = 0$ and $S = 1$ in AFM rings [6], while they have $S = 5/2$ and $S = 7/2$ in the Mn 3×3 grid [7]. In rings and grids the anisotropic terms in Eq. (1) have no qualitative effects for most observables, including those on which we here focus. In view of this, and since numerical calculations based on the full Hamiltonian equation (1) are cumbersome, in these two classes of systems we will use Eq. (1) neglecting the anisotropic terms. In addition, large-scale numerical techniques must be used for Mn 3×3 .

Our first goal is the calculation of the damping of equilibrium fluctuations of the molecule magnetization $M(t) \equiv gS_z$ due to interactions of the electron spins with a heat bath. We adopt the well established framework presented in [8] for the irreversible evolution of the density matrix $\rho_{st}(t)$ [in the representation of the *exact* eigenstates

of (1)] in the presence of a heat bath. Here we focus on time scales τ much longer than the typical periods of free evolution of the system [$2\pi\hbar/(E_s - E_t)$, with E_s and E_t eigenvalues of (1)]. In this case, the so-called ‘‘secular approximation’’ enables the time evolution of the off-diagonal matrix elements $\rho_{s\neq t}(t)$ to be decoupled from that of the diagonal elements $\rho_{ss}(t) := p_s(t)$. In a frequency-domain picture (e.g., the outcome of a scattering experiment), this corresponds to a clear separation of inelastic (IE) and quasielastic (QE) spectral contributions. Then the (single-Lorentzian) broadening of IE transitions merely reflects the lifetimes of the involved pair of levels (determined by Fermi’s golden rule applied to the spin-bath interaction). These IE off-diagonal contributions to the evolution equations for $M(t)$ will be neglected since we are here interested in the subtler QE components of the dynamics. Only the latter are detected by low-frequency probes such as ac susceptibility or NMR.

In the secular approximation the populations of the molecular eigenstates, $p_s(t)$, evolve through the well known rate (master) equations

$$\dot{p}_s(t) = \sum_t W_{st} p_t(t), \quad (2)$$

where W_{st} is the st element of the rate matrix \mathbb{W} , i.e., the probability per unit time that a transition between levels $|t\rangle$ and $|s\rangle$ is induced by the interaction with the heat bath ($W_{ss} = -\sum_t W_{ts}$).

We are here focusing on temperatures for which relaxation is determined by interactions of the spin degrees of freedom of each molecule with the crystal phonon heat bath. Since we are interested in general qualitative features of the relaxation dynamics and not in compound-specific details, we will assume a unique simple form for the spin-phonon coupling for all compounds. The main contribution to this coupling comes from the modulation of the local rank-2 crystal fields $\sum_i \sum_q b_2^q(i) O_2^q(\mathbf{s}_i)$ by phonons. This leads to the following spin-phonon coupling potential

$$V = \sum_{l=1,N} \sum_{Q=-2,2} \sum_{\mathbf{k}\sigma} C_Q(l, \mathbf{k}, \sigma) O_2^Q(\mathbf{s}_l) (c_{\mathbf{k}\sigma} + c_{-\mathbf{k}\sigma}^\dagger), \quad (3)$$

where $C_Q(l, \mathbf{k}, \sigma)$ is the coupling constant between the Q -type electric quadrupole on ion l [$O_2^Q(\mathbf{s}_l)$], and phonon modes of wave vector \mathbf{k} and branch index σ . As usual [9], we adopt a Debye model for phonons, and for the sake of simplicity we assume $Q = 0, 1, 2$ with $C_Q(l, \mathbf{k})$ independent of l and Q . We have checked that the results do not change qualitatively if different choices are made, although compound-specific $C_Q(l, \mathbf{k}, \sigma)$ would be needed for precise quantitative calculations, which are beyond the aim of this Letter. The rate matrix \mathbb{W} appearing in Eq. (2) can be calculated by first-order perturbation theory applied to V , leading to

$$W_{st} = \gamma\pi \langle t | \sum_{i=1,N} \sum_{Q=0,1,2} O_2^Q(\mathbf{s}_i) |s\rangle|^2 \Delta_{st}^3 n(\Delta_{st}), \quad (4)$$

with $n(x) = (e^{\beta\hbar x} - 1)^{-1}$, $\Delta_{st} = (E_s - E_t)/\hbar$. In our simplified spin-phonon model γ is the unique free parameter and describes the spin-phonon coupling strength. It will be determined by comparison with experimental data. The next step is the calculation of the Fourier transform $S_{\mathcal{A},\mathcal{B}}(\omega)$ of the cross-correlation function $\langle \Delta \mathcal{A}(t) \Delta \mathcal{B}(0) \rangle$ implied by Eq. (2) for equilibrium fluctuations of two generic observables \mathcal{A}, \mathcal{B} . We exploit the fluctuation-dissipation theorem, which implies

$$S_{\mathcal{A},\mathcal{B}}(\omega) = \frac{2k_B T \chi''_{\mathcal{A},\mathcal{B}}(\omega)}{\omega} = 2k_B T \tilde{R}'_{\mathcal{A},\mathcal{B}}(i\omega), \quad (5)$$

with $\chi''_{\mathcal{A},\mathcal{B}}(\omega)$ the imaginary part of the susceptibility, and $\tilde{R}'_{\mathcal{A},\mathcal{B}}(z)$ the real part of the Laplace transform of the relaxation function $R_{\mathcal{A},\mathcal{B}}(t)$. The latter is defined as $\lim_{\epsilon \rightarrow 0} [\langle \mathcal{A}(t) \rangle - \langle \mathcal{A} \rangle^{\text{eq}}] / \epsilon$, with a perturbation $\epsilon \mathcal{B}$ abruptly switched off at $t = 0$. We have calculated $R_{\mathcal{A},\mathcal{B}}(t)$ by solving the system of Eq. (2), obtaining the following expression:

$$S_{\mathcal{A},\mathcal{B}}(\omega) = \sum_{q,t} (\mathcal{B}_{tt} - \langle \mathcal{B} \rangle^{\text{eq}}) \times (\mathcal{A}_{qq} - \langle \mathcal{A} \rangle^{\text{eq}}) \text{Re} \left[p_t^{\text{eq}} \left(\frac{1}{i\omega - \mathbb{W}} \right)_{qt} \right], \quad (6)$$

where p_t^{eq} is the equilibrium population of the t th level, and $\mathcal{B}_{tt} = \langle t | \mathcal{B} | t \rangle$. This leads to correlations decaying as a sum of exponentials with n characteristic times $\tau_{\text{QE}}^{(i)}$ given by the inverse eigenvalues of $-\mathbb{W}$, n being the dimension of the molecule spin Hilbert space. Therefore, the QE frequency spectrum is in general a sum of Lorentzians centered at zero frequency having width $1/\tau_{\text{QE}}^{(i)}$. It should be stressed that the n $\tau_{\text{QE}}^{(i)}$ cannot be directly determined from the n level lifetimes $\tau_{\text{life}}^{(s)}$. Although both $\tau_{\text{QE}}^{(i)}$ and $\tau_{\text{life}}^{(s)}$ contain integrated information on the spin-bath dissipation channels, this information is different for the two sets. Thus, low-frequency measurements probing the QE dynamics provide different and complementary information with respect to direct lifetime measurements by high-frequency techniques (e.g., inelastic neutron scattering).

We focus now on the important case $\mathcal{A} = \mathcal{B} = S_z$, i.e., we study the spectrum of fluctuations of the cluster magnetization. In general, many different $1/\tau_{\text{QE}}^{(i)}$ may be expected to contribute to this spectrum, i.e.,

$$S_{S_z, S_z}(\omega, T, B) = \sum_{i=1,n} A(\lambda_i, T, B) \frac{\lambda_i(T, B)}{\lambda_i(T, B)^2 + \omega^2}, \quad (7)$$

where $\lambda_i(T, B) \equiv 1/\tau_{\text{QE}}^{(i)}$. Figure 1 shows intensity plots of the frequency weights $A(\lambda_i, T, B)$ of the magnetization autocorrelation, calculated from Eq. (6), as a function of temperature T for three representative systems. The single free parameter γ has been estimated by the observed peak in the T dependence of the NMR $1/T_1$ (see below), apart from Fe_8 for which relaxation data allow to fix γ directly.

The calculations reported in Fig. 1 show that for a fairly wide range of values of T and B , a single frequency $\lambda_0(T, B)$ (and therefore a single Lorentzian) dominates the spectrum in the three classes of molecules we considered (AFM rings, AFM grids and nanomagnets). The dominating frequency λ_0 is different from the lifetime broadening of any level. In the special case of nanomagnets (Fe_8 , Mn_{12}), the calculated λ_0 coincides with the smallest λ_i . Hence, in this case λ_0^{-1} is also the time determining the asymptotic return to equilibrium of the magnetization when the nanomagnet is prepared in a highly nonequilibrium state by a strong applied field. Instead, our calculations show that in rings and grids λ_0 is orders of magnitude larger than the smallest λ_i (the latter is not visible in Fig. 1 since the associated weight is tiny). AFM rings are characterized by a single dominating characteristic frequency λ_0 for $B \ll B_c$ with B_c the field at which an $S = 1$ level crosses $S = 0$, and for $T \lesssim 12J/N$. This corresponds to the regime in which the magnetization and its fluctuations are mainly determined by levels belonging to the $S = 1$ manifold. In this single-frequency regime, the decay of fluctuations takes places mostly through indirect Orbach-like

processes involving higher-lying S manifolds, resulting in an approximately exponential dependence in $1/T$ of λ_0 (see Fig. 1). A different T dependence occurs at low T , where direct transitions within the field-split $S = 1$ manifold constitute the main relaxation mechanism. Fe_8 is also characterized by a single dominating characteristic frequency λ_0 , depending exponentially on $1/T$, if the Zeeman energy is small with respect to the anisotropy barrier. Finally, the $\text{Mn } 3 \times 3$ grid is again characterized by a dominating frequency for $B \ll B_c$ with B_c the field at which an $S = 7/2$ level crosses $S = 5/2$, and for $T \lesssim \Delta/k_B$, with $\Delta \sim 0.9$ meV the exchange gap. Therefore, for all these systems the calculated dynamical structure factor of Eq. (7) is dominated by a single contribution:

$$S_{S_z, S_z}(\omega, T, B) \simeq A(\lambda_0, T, B) \frac{\lambda_0(T, B)}{\lambda_0(T, B)^2 + \omega^2}. \quad (8)$$

From linear-response theory $A(\lambda_0, T, B) \propto \chi(B, T)T$, with $\chi(B, T)$ the static Curie susceptibility. Therefore, a measurement of S_{S_z, S_z} allows the T and B dependence of $\lambda_0(T, B)$ to be extracted straightforwardly. In the following we will show that NMR confirms this picture and allows $\lambda_0(T, B)$ to be determined.

The nuclear spin-lattice relaxation rate $1/T_1$ is given by a linear combination of the Fourier transforms of electronic spin correlation functions $S_{S_{i,\alpha}, S_{j,\beta}}$ (evaluated at the Larmor frequency $\omega_L(B)$) [10]. Within this framework, $1/T_1$ is given by a linear combination of the Fourier transforms of electronic spin correlation functions $S_{S_{i,\alpha}, S_{j,\beta}}$, evaluated at the Larmor frequency $\omega_L(B)$. Since $\omega_L \ll \Delta_{st}$, only the QE part of these correlations contributes to $1/T_1$. If anisotropy is neglected, Eq. (6) shows that only the $\alpha = \beta = z$ terms are nonzero because $\langle t|s_{i,x}|t \rangle = \langle t|s_{i,y}|t \rangle = 0$. In addition, for a magnetic ring $\langle t|s_i^z|t \rangle = \langle t|s_j^z|t \rangle = 1/N \langle t|S_z|t \rangle$, where S_z is the z component of the total spin operator \mathbf{S} . Then,

$$1/T_1 = G S_{S_z, S_z}(\omega_L), \quad (9)$$

where G is a scale factor depending only on the positions and spins of the probed nuclei. The same result holds also for grids as long as the ground multiplet gives the main contribution (i.e., at sufficiently low T). In fact, in this regime all $S_{S_{i,z}, S_{j,z}}(\omega) \propto S_{S_z, S_z}(\omega)$. We have numerically checked that this holds approximately in the single-Lorentzian regime (see Fig. 1). If magnetic anisotropy cannot be neglected, as in the case of Fe_8 , the simple result of Eq. (9) can be recovered if \mathbf{B} is along the easy axis, by exploiting the fact that within the ground S multiplet $S_{S_{i,z}, S_{j,z}}(\omega) \propto S_{S_z, S_z}(\omega)$. Therefore, in all these systems NMR measurements of $1/T_1$ can be used as a probe of $S_{S_z, S_z}(\omega)$.

Equations (8) and (9) imply that, as a function of T , $1/T_1/(\chi T)$ should display a single peak when $\lambda(T, B) = \omega_L(B)$. Moreover, since $\lambda(T, B)$ depends little on B for not too large B , $1/T_1/(\chi T)$ measured on different nuclei and by setting the value of B in order to keep $\omega_L(B)$ fixed,

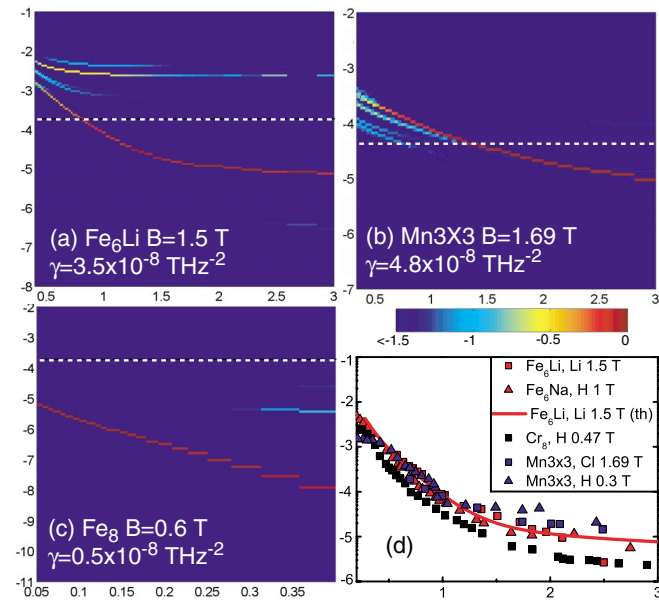


FIG. 1 (color). Calculated frequency weights $A(\lambda_i, T, B)$ of the magnetization autocorrelation vs Δ/T (a,b), with Δ the exchange gap, or vs $1/T$ (c) (x axis). The y axis is $\log_{10}(\lambda)$ (in THz). The color maps $\log_{10}[A(\lambda_i, T, B)/(\chi T)]$ [see Eq. (7)]. The Hamiltonian parameters are given in [5–7]. For each value of T , the spectra have been normalized by χT , which is proportional to the size of equilibrium fluctuations. The white dashed lines are the ${}^7\text{Li}$ (a), ${}^{35}\text{Cl}$ (b), and ${}^1\text{H}$ (c) Larmor angular frequencies. The results for Cr_8 (not shown) are similar to those of Fe_6Li , with $\gamma = 5 \times 10^{-7} \text{ Thz}^{-2}$. (d) shows the characteristic frequency λ_0 vs Δ/T for Cr_8 , Fe_6Li , Fe_6Na , and $\text{Mn } 3 \times 3$ extracted from the experimental $1/T_1$ data (see text). The data are taken from Ref. [3], apart from those for $\text{Mn } 3 \times 3$ which are new. The red line represents the dominant frequency λ_0 of Fe_6Li deduced from panel (a).

should display a peak at approximately the same T . This is clearly visible, for instance, in our calculations of $1/T_1/(\chi T)$ for Fe_6Li on Li and H nuclei, shown in Fig. 2, which contains our calculated T dependence of $1/T_1$. By increasing B by a factor p and keeping the nucleus fixed, the peak value of $1/T_1/(\chi T)$ should decrease by about p . This can be seen in Fig. 2 in the calculated curves for Cr_8 . This is what had been experimentally observed in [3], where a phenomenological single-Lorentzian expression for the Larmor-frequency dependence of $1/T_1$ had been shown to fit NMR data in several AFM rings very well. Part of the data are included in the lower panel of Fig. 2 together with new data we collected on the $\text{Mn } 3 \times 3$ grid. The agreement with our calculations is very good. In addition, Fig. 1(d) contains the T dependence of the characteristic frequency λ_0 extracted from the Lorentzian fit of the data [3]. The results are in good agreement with the behavior of the calculated λ_0 in Figures 1(a) and 1(b). Similar agreement is obtained for the Cr_8 ring. We remark that in the T range, where the peak in $1/T_1$ occurs the calculated T dependence of λ_0 is nearly exponential in $1/T$ (relaxation through intermultiplet Orbach processes), and in good agreement with experimental data. Hence, the power-law T dependence assumed in [3], although fitting the data over a limited temperature range, is not confirmed by our microscopic calculation. In the case of Fe_8 , the free parameter γ has been fixed in order to reproduce the T dependence of the relaxation time of the magnetization in the thermally activated regime measured in [11]. There is therefore no free parameter in the calculation. As can be seen in Fig. 1, the calculated $\lambda_0(T)$ is much smaller than the ^1H Larmor frequency. Indeed, measured $1/T_1$ data do not show a peak [12], and are in good agreement with our parameter-free calculations reported in the inset of Fig. 2.

In conclusion, a general expression for the quasielastic part of the dynamic structure factor in the presence of a heat bath has been derived, starting from the master equation applied to the full microscopic Hamiltonian. By specializing this expression to the case of the total molecule magnetization, we have calculated (Fig. 1) the frequency spectral weights of the decay of fluctuations of this observable. We have shown that in AFM rings, grids, and nanomagnets the decay of equilibrium fluctuations due to interactions with phonons is characterized by a single characteristic frequency $\lambda_0(T, B)$ over a wide range of temperatures and fields. We have also shown that the NMR spin-lattice relaxation rate $1/T_1$ can be used to measure $\lambda_0(T, B)$. This microscopic result differs from the previous phenomenological models of $1/T_1$ in rings [3] and nanomagnets [12], where $1/T_1$ was assumed to probe level lifetimes in the presence of phonons, and not a relaxation time. Our calculations are in good agreement with existing experimental NMR data, and with our new measurements on the $\text{Mn } 3 \times 3$ grid.

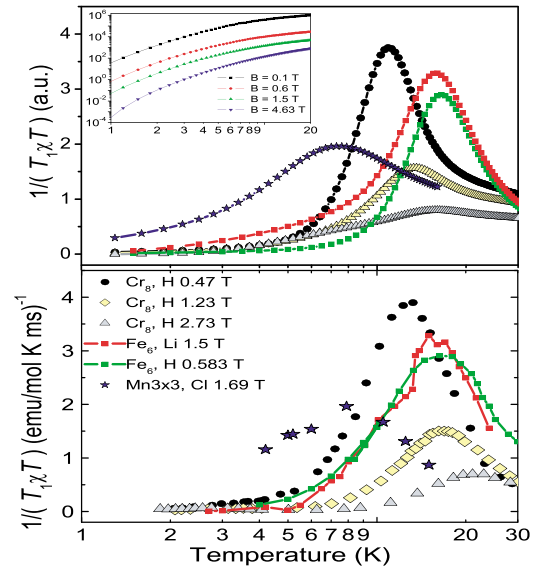


FIG. 2 (color). Top: calculated $1/T_1/(\chi T)$ as a function of the temperature T for Cr_8 , Fe_6Li , and $\text{Mn } 3 \times 3$ for different fields and nuclei. Inset: Calculated $1/T_1(T)$ (in a.u.) for Fe_8 for different values of B applied along the easy axis. Bottom: Measured $1/T_1/(\chi T)$ vs T for Cr_8 , Fe_6Li , and $\text{Mn } 3 \times 3$. In order to fit the figure, data for Fe_6Li were divided by 3, and those for $\text{Mn } 3 \times 3$ by 5.

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