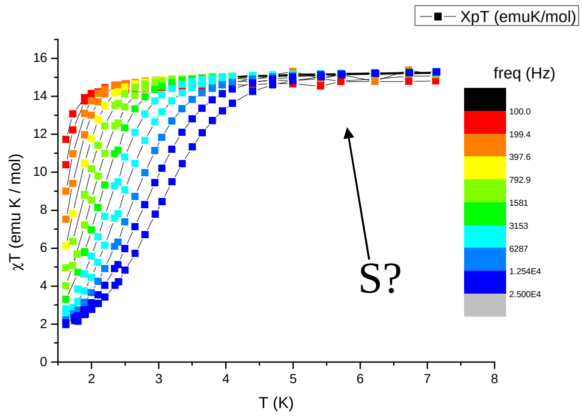
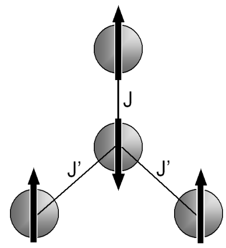
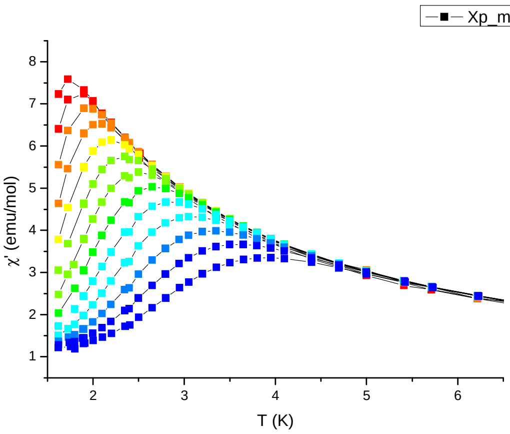
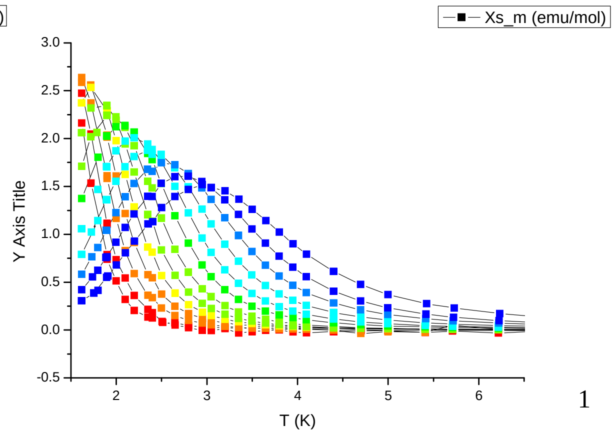
Fe4 Single Molecule Magnets



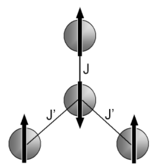


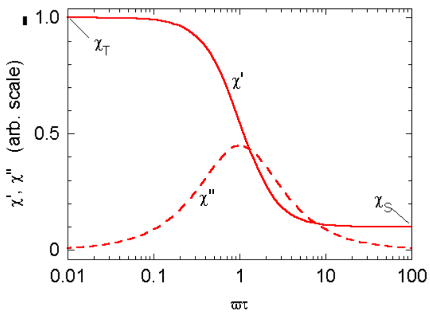
χac vs. T a diverse frequenze
È corretto estrarre τ=f(T) dai max
In χ" solo se decresce molto
rapidamente con T



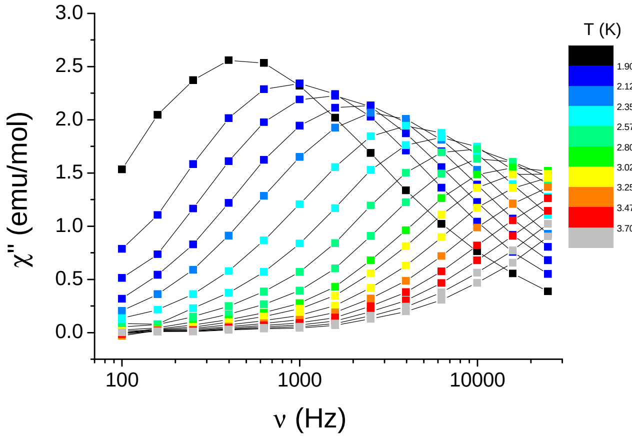


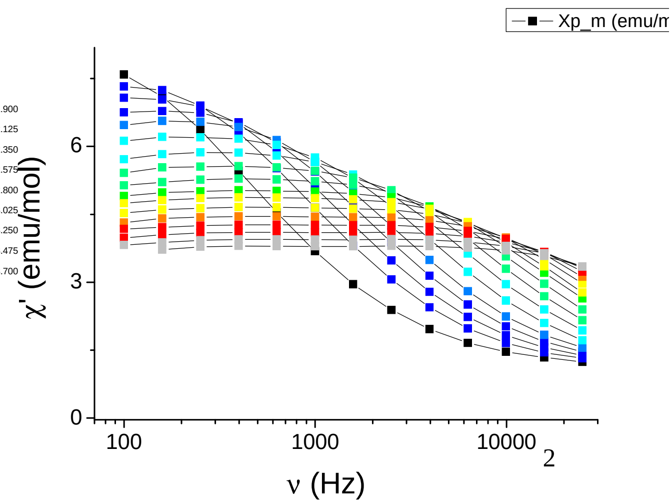
Fe4 Single Molecule Magnets



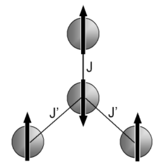


τ=f(T) da dati χ_{ac} dovrebbe
Sempre essere estratto riportando χ_{ac} vs. ν
a diverse temperature, e usando il modello
di Debye

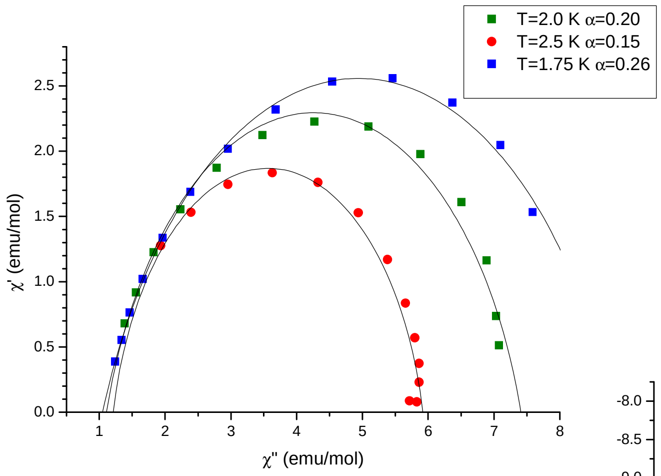




Fe4 Single Molecule Magnets



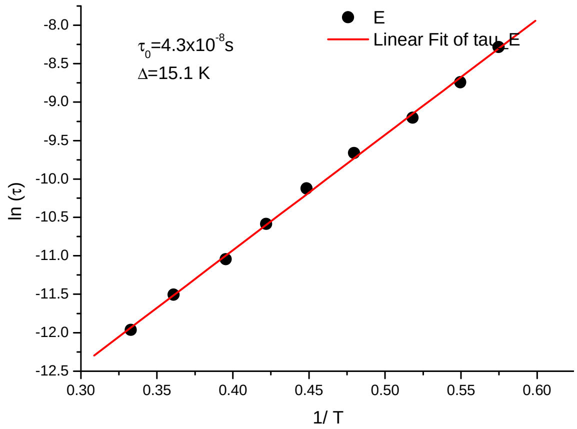
Argand (Cole-Cole) plot



[2/2/2007 13:18 "/Graph4" (2454133)]
Linear Regression for tau_E:
Y = A + B * X

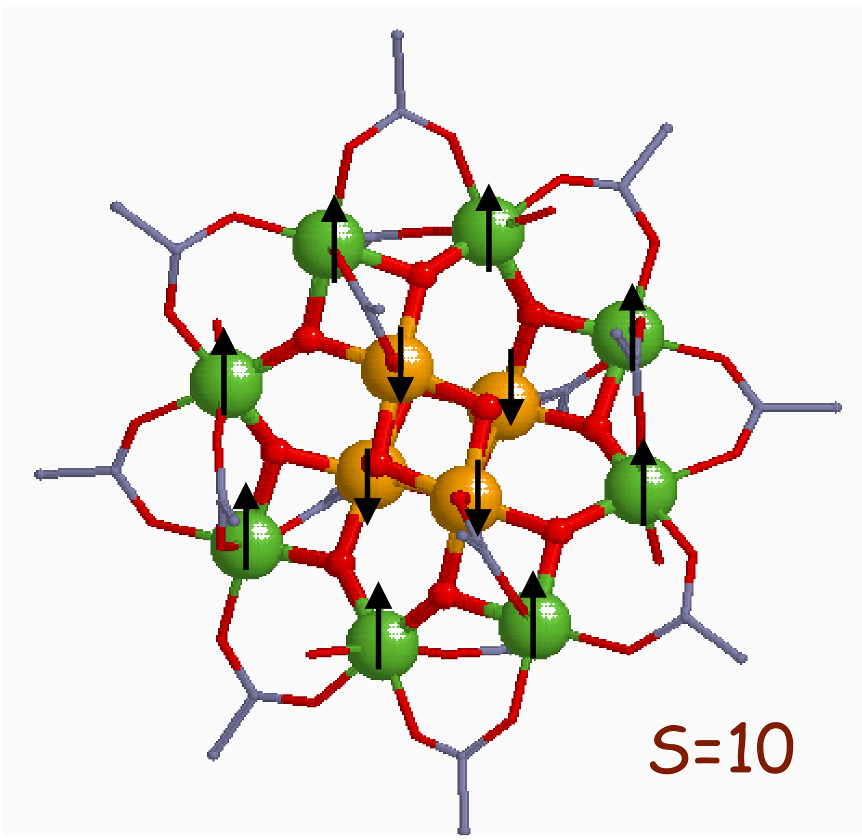
Parameter	Value	Error
A	-16.96907	0.1301
B	15.07782	0.28234

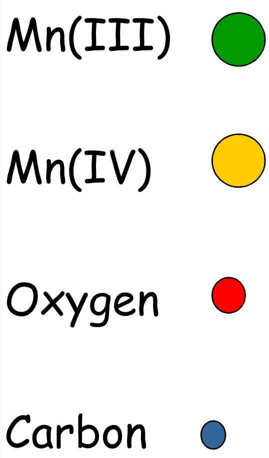
R	SD	N	P
0.99878	0.06666	9	<0.0001



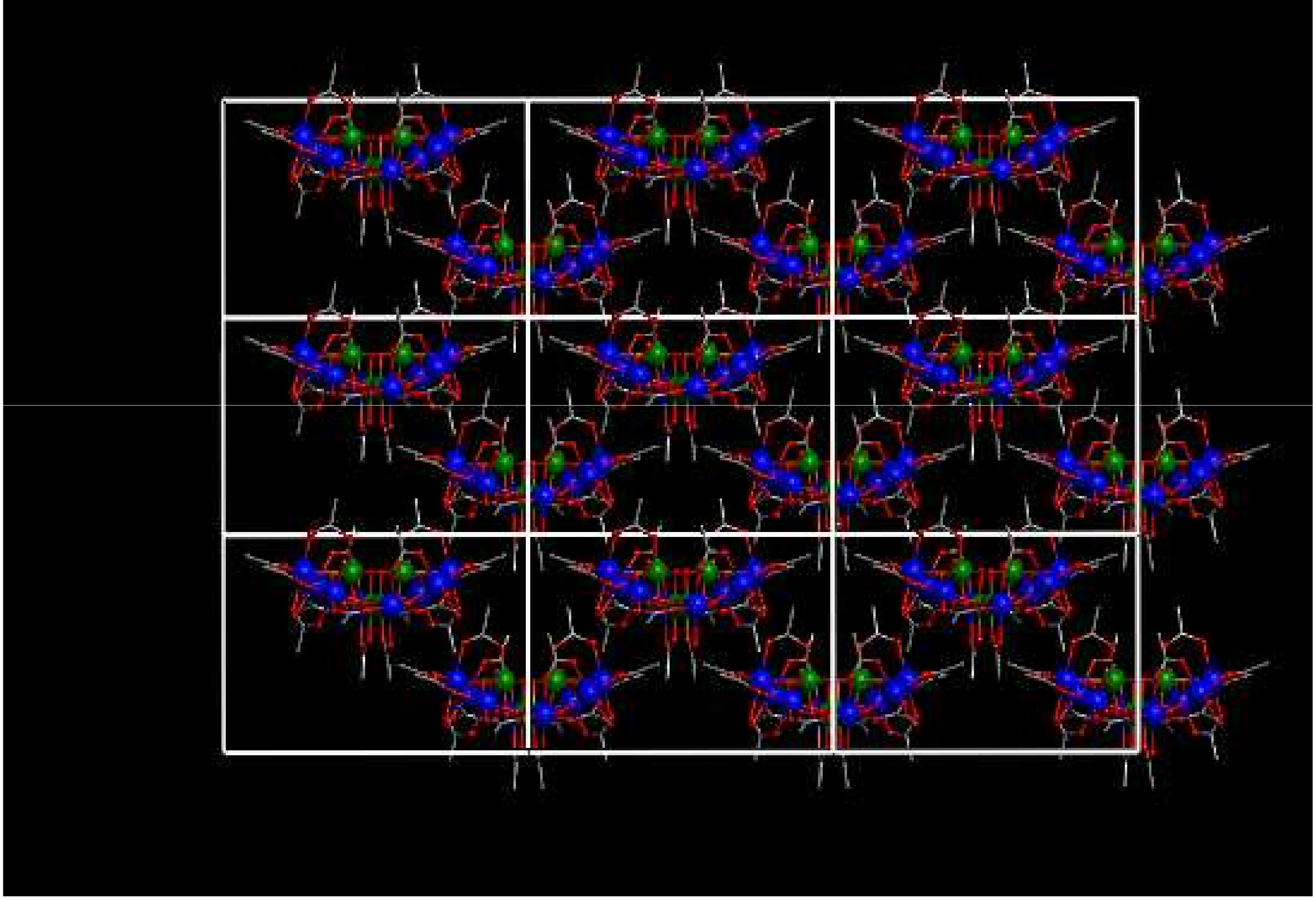
Arrhenius plot

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4].2CH_3COOH.4H_2O$

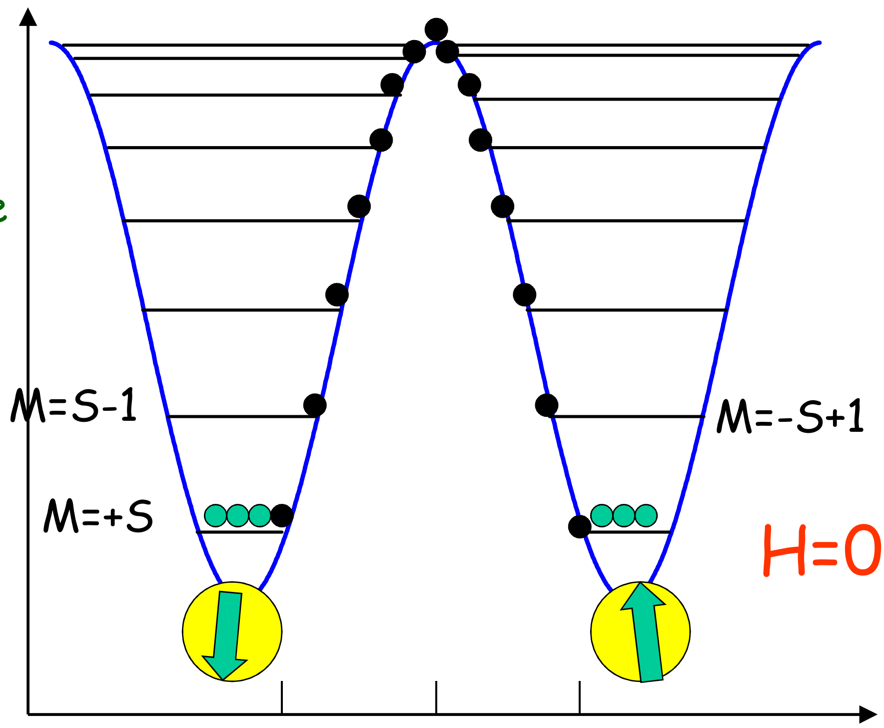




The molecules are regularly arranged in the crystal

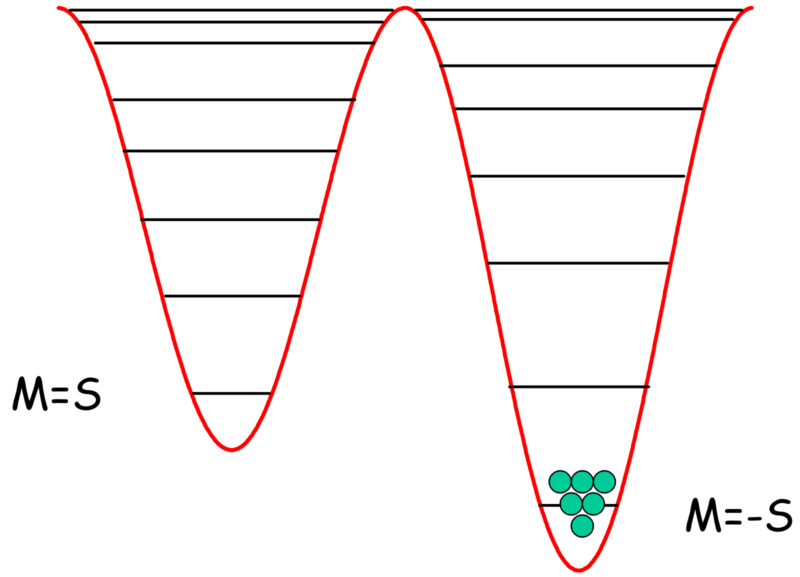


Double well potential $\mathcal{H}=DS_z^2$ (D<0)



$$\mathcal{H} = DS_z^2 + g\mu_B H_z S_z$$

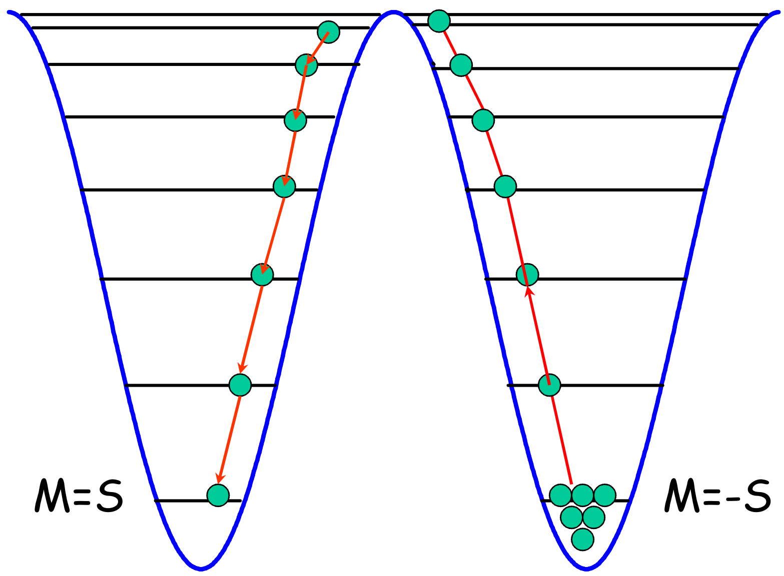
H≠0



return to the equilibrium

thermal activated mechanism

H=0

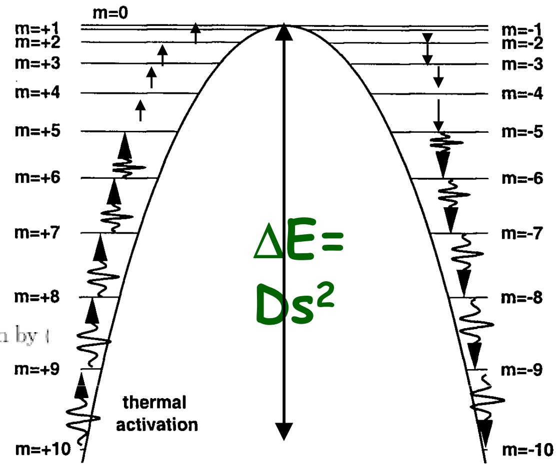


Energy barrier given by uniaxial magnetic anisotropy

$$\mathcal{H}_{an} = DS_z^2$$

$$S_z \mid m\rangle = m \mid m\rangle$$

$$E_m = -|D|m^2$$



At equilibrium, the probability p_m^0 that the spin is in state $|m\rangle$ is given by

$$p_m^0 = (1/Z)\exp[-\beta(E_m)]$$

Intuitively, it may be expected that the relaxation rate $1/\tau$ is proportional to the probability to be at the top of the barrier.

$$1/\tau = (1/\tau_0)p_0^0 = (1/Z)(1/\tau_0)\exp(-\beta E_0) \approx$$

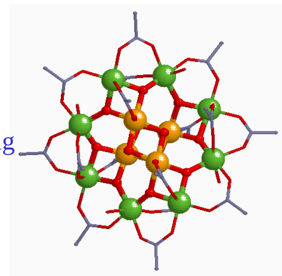
$$\approx (1/\tau_0)\exp[-\beta(E_0 - E_s)] \approx (1/\tau_0)\exp(-\beta|D|s^2)$$

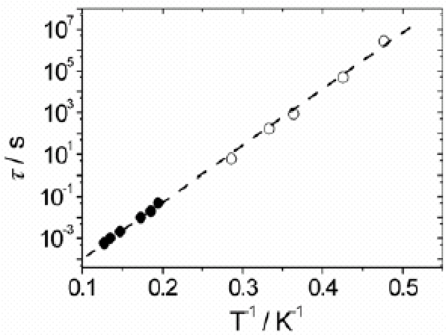
$$\tau=\tau_0\exp(\Delta E/k_BT)$$

$[Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4].2CH_3COOH.4H_2O$

Table 4.1. Magnetic anisotropy parameters of Mn_{12}ac evaluated from four different experiments.

D (K)	B_4^0 (K)	B_4^4 (K)	Ref	
-0.66(2)	$-3.2(2)x10^{-5}$	$\pm6(1)x10^{-5}$	(Barra *et al.* 1997a)	EPR
-0.657(2)	$-3.35(6)x10^{-5}$	$\pm4.3(7)x10^{-5}$	(Mirebeau *et al.* 1999)	Neutron scattering
-0.68	$-2.9x10^{-5}$	$-1.2x10^{-4}$	(Hill *et al.* 1998)	EPR
-0.66	$-3.4x10^{-5}$	-	(Cornia *et al.* 2000)	Torque





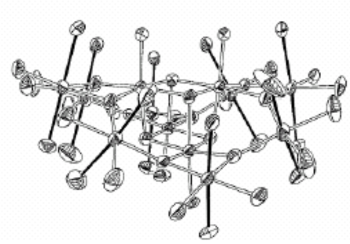
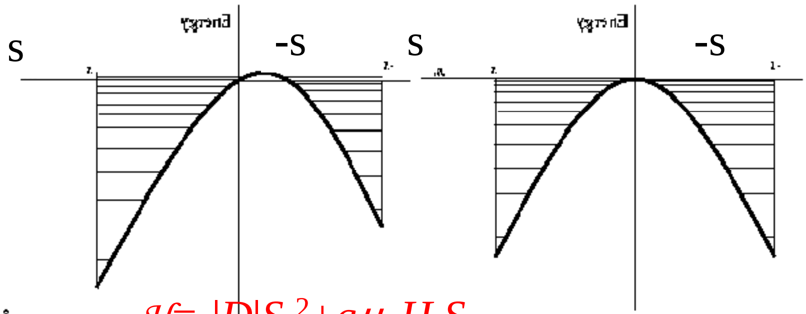


Figure 4.25. Temperature dependence of the relaxation time in log scale of Mn_{12}ac extracted from ac susceptibility data (solid symbols) in the frequency range 1-270 Hz and from time decay of the magnetisation (empty symbols). The line corresponds to the Arrhenius law $\tau=\tau_0\exp(\Delta E/T)$ with τ_0 $=2.1\times10^{-7}$ s and ΔE=62 K.

Classic effect of a longitudinal field on the energy barrier:



$\mathcal{H}=-|D|S_z^2+g\mu_B H_z S_z$

$$E_m^{(0)} = -|D|m^2 + g\mu_B H_z m$$

The energy is at a maximum when: $m_{max} = (g\mu_B H_z)/(2|D|)$

$$2|D|m = g\mu_B H_z$$

$$E_{max} = (g\mu_B H_z)^2/(4|D|)$$

$$E_{-s} = -|D|s^2 + g\mu_B H s$$

$$k_B T_0 \approx |D|s^2 - g\mu_B H s + (g\mu_B H)^2/(4|D|) = |D|[s - g\mu_B H/(2|D|)]^2$$

The field reduces the height of the barrier for the particles that are
In the "wrong" well

Transition Probabilities and master equation

The time evolution of the population of the |m> state is given by:

$$\frac{d}{dt}p_m(t) = \sum_q \left[\gamma_q^m p_q(t) - \gamma_m^q p_m(t)\right]$$

Where γ are the transition probabilities independent from each other (Markov process)
And are related to spin-phonon interactions.

A trivial solution is that at equilibrium: $p_m^0 = (1/Z)\exp(-\beta E_m)$

$$\sum_q \left[\gamma_q^m p_q^0 - \gamma_m^q p_m^0\right] = 0$$

The detailed balance principle tell us that also each term of the sum vanishes at equilibrium $\gamma_m^{m'} p_m^0 = \gamma_{m'}^m p_{m'}^0$

$$\gamma_m^{m'}/\gamma_{m'}^m = p_{m'}^0/p_m^0 = \exp[\beta(E_m - E_{m'})]$$

Solution of the master equation

In a more general case (biaxial anisotropy, transverse field)

$$| m^* \rangle = \sum_{m'} \varphi_{m'}^{(m)} \, | m' \rangle$$

With k=0,1, 2..,2s.
The population of each state varies exponentially:

$$p_m(t) = \varphi_m^{(k)} \exp(-t/\tau_k)$$

And substituting in $\displaystyle \frac{d}{dt} p_m(t) = \sum_q \left[\gamma_q^m p_q(t) - \gamma_m^q p_m(t) \right]$

$$\frac{1}{\tau_k} \varphi_m^{(k)} = \sum_q \left[\gamma_q^m \varphi_q^{(k)} - \gamma_m^q \varphi_m^{(k)} \right] = \sum_q \left[\gamma_q^m - \delta_q^m \sum_{q'} \gamma_m^{q'} \right] \varphi_q^{(k)}$$

where the Kronecker symbol δ_q^m (=1 if $q = m$, while $\delta_q^m = 0$ if $q \neq m$) has been introduced.

the master matrix

$$\Gamma_q^m = \gamma_q^m - \delta_q^m \sum_{m'} \gamma_{m'}^m$$

$$\boxed{\frac{d\vec{N}}{dt} = \tilde{\Gamma} \vec{N}}$$

$$\tilde{\Gamma} = \begin{pmatrix} -\sum_{m' \neq 1} \gamma_1^{m'} & \gamma_2^1 & \cdot & \cdot & \gamma_{2s+1}^1 \\ \gamma_1^2 & -\sum_{m' \neq 2} \gamma_2^{m'} & \cdot & \cdot & \gamma_{2s+1}^2 \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot & \cdot \\ \gamma_1^{2s+1} & \gamma_2^{2s+1} & \cdot & \cdot & -\sum_{m' \neq s} \gamma_{2s+1}^{m'} \end{pmatrix} \qquad \vec{N} = \begin{pmatrix} N_1 \\ N_2 \\ \cdot \\ \cdot \\ N_{2S+1} \end{pmatrix}$$

There are 2s+1 solution of **($\det\Gamma$-λ)=0**
One solution is λ=0, corresponding to $\tau=\infty$ (the equilibrium)

The relaxation rate at low temperature is $\displaystyle \tau = \max_{\lambda_i \neq 0} \left\{ -\frac{1}{\lambda_i} \right\}$

$$\frac{d(\vec{P}-\vec{P}_{eq})}{dt} = \frac{d\vec{P}}{dt} = \begin{pmatrix} \lambda_1 & & & \\ & \cdot & & \\ & & \cdot & \\ & & & \lambda_{2S+1} \end{pmatrix} \vec{P}$$

$$\gamma_m^p = \frac{2\pi}{\hbar} \sum_{q,\sigma} \left| \left\langle pn_{q,\sigma} \mp 1 \middle| H_{spin-phonon} \middle| mn_{q,\sigma} \right\rangle \right|^2 \delta(E_p - E_m \mp \hbar\omega_{q,\sigma})$$

the spin-phonon interaction

local rotations and local strains produce a time-dependent modification (or `modulation') of the anisotropy energy. The new terms of the Hamiltonian induce transitions between the eigenstates |*m**> of the static Hamiltonian

$$H_{spin-phonon} = g_1\varepsilon_{xx}S_x^2 + g_2\varepsilon_{yy}S_y^2 + \frac{1}{2}\left(g_3\varepsilon_{xy}\{S_x,S_y\} + g_4\varepsilon_{xz}\{S_x,S_z\} + g_5\varepsilon_{yz}\{S_y,S_z\}\right) + \frac{1}{2}\left(g_6\omega_{xy}\{S_x,S_y\} + g_7\omega_{xz}\{S_x,S_z\} + g_8\omega_{yz}\{S_y,S_z\}\right)$$

Where $\varepsilon_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial j} + \frac{\partial u_j}{\partial i}\right)$ is the simmetric

And $\omega_{ij} = \frac{1}{2}\left(\frac{\partial u_i}{\partial j} - \frac{\partial u_j}{\partial i}\right)$ is the antisymmetric part of the deformation tensor

With $\{\hat{A},\hat{B}\} = \hat{A}\hat{B} + \hat{B}\hat{A}$ and $i,j = x,y,z$

In a more quantitative way

$$\gamma_m^p = \frac{3}{2\pi\rho\hbar^4 c^5} \frac{(E_p - E_m)^3}{e^{\beta(E_p - E_m)} - 1} \left\{ g_a \left[(S_+^2)_{mp}^2 + (S_-^2)_{mp}^2 \right] + g_b \left[(\{S_+, S_z\})_{mp}^2 + (\{S_-, S_z\})_{mp}^2 \right] \right\}$$

The allowded transitions for spin-phonon coupling have

|m-m'|=1,2

The detailed balance is satisfied

$$\gamma_p^m = \frac{3}{2\pi\rho\hbar^4 c^5} \frac{(E_m - E_p)^3}{e^{\beta(E_m - E_p)} - 1} \left\{ g_a \left[(S_+^2)_{mp}^2 + (S_-^2)_{mp}^2 \right] + g_b \left[(\{S_+, S_z\})_{mp}^2 + (\{S_-, S_z\})_{mp}^2 \right] \right\} =$$

$$= \frac{3}{2\pi\rho\hbar^4 c^5} \frac{(E_p - E_m)^3}{-e^{\beta(E_m - E_p)} + 1} \left\{ g_a \left[(S_+^2)_{mp}^2 + (S_-^2)_{mp}^2 \right] + g_b \left[(\{S_+, S_z\})_{mp}^2 + (\{S_-, S_z\})_{mp}^2 \right] \right\} = \gamma_m^p e^{\beta(E_m - E_p)}$$

When (E_m-E_p) is small (which also corresponds to the top of the barrier) the transition probability is small because of the factor $(E_m-E_p)^3$, which mainly refects the fact that there are few phonon states of very low energy.

$$\gamma_q^p = \frac{3v}{\pi\hbar^4 M c_s^5} \frac{(E_p - E_q)^3}{\exp[\beta(E_p - E_q) - 1]}$$
$$\left\{ |\tilde{D}_a|^2 \left[\left|\langle p \mid S_+^2 \mid q\rangle\right|^2 + \left|\langle p \mid S_-^2 \mid q\rangle\right|^2 \right] + |\tilde{D}_b|^2 \left[|\langle p \mid \{S_+, S_z\} \mid q\rangle|^2 + |\langle p \mid \{S_-, S_z\} \mid q\rangle|^2 \right] \right\} \qquad \text{(F.23)}$$

where E_p and E_q are the eigenvalues corresponding to $\mid p^*\rangle$ and $\mid q^*\rangle$, $\tilde{D}_a$ and $\tilde{D}_b$ are spin–phonon coupling coefficients,

$$\langle p \mid S_+^2 \mid q\rangle = \sum_{mm'} (\varphi_p^{m'})^* \varphi_q^m \langle m' \mid S_+^2 \mid m\rangle$$
$$= \sum_m (\varphi_p^{m+2})^* \varphi_q^m \sqrt{[s(s+1) - m(m+1)][s(s+1) - (m+2)(m+1)]}$$
$$= \langle q \mid S_-^2 \mid p\rangle^* \qquad \text{(F.24)}$$

and

$$\langle p \mid \{S_+, S_z\} \mid q\rangle = \sum_{mm'} (\varphi_p^{m'})^* \varphi_q^m \langle m' \mid \{S_-, S_z\} \mid m\rangle$$
$$= \sum_m (2m+1)(\varphi_p^{m+1})^* \varphi_q^m \sqrt{[s(s+1) - m(m+1)]}$$
$$= \langle q \mid \{S_-, S_z\} \mid p\rangle^* . \qquad \text{(F.25)}$$

In a more quantitative way

$$1/\tau \approx \frac{k_B}{c_s^5}\frac{v}{M}\left(\frac{k_B}{\hbar}\right)^4\left(\frac{\delta E}{k_B}\right)^3\left(\frac{|D|s^2}{k_B}\right)^2 \exp[-\beta(E_0 - E_{-s})]$$

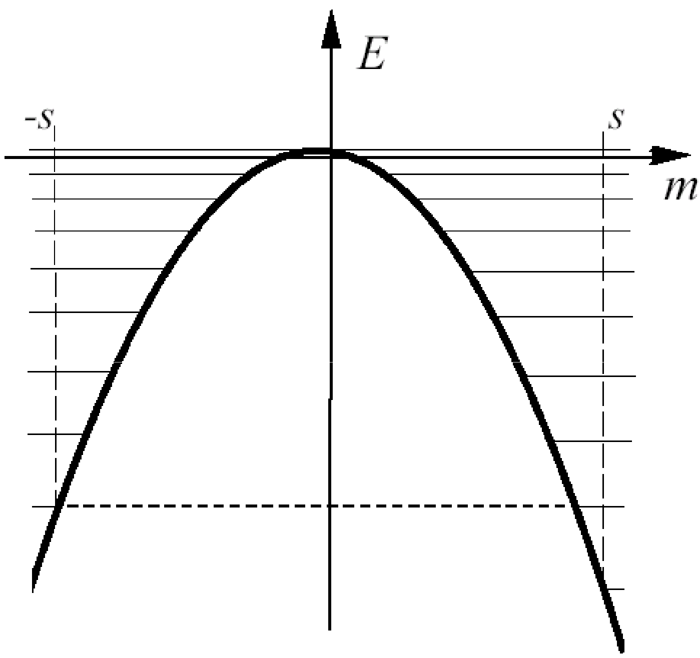
where $\delta E = E_0 - E_1 = |D| = 0.6$ K for Mn12ac, and $E_0 - E_s = 60$K .
The order of magnitude of the sound velocity is, to our knowledge, not known.
Since it appears with the power 5, this is the main cause of uncertainty.
Tentatively, with the value c_s =1000m/s, the ratio v=M will be taken equal to 0.001 m3/kg, as for water. This yields (in seconds)

$$\tau \approx 10^{-7} \exp\frac{T_0}{T}$$

The role of photons is much less imporant because:

$$\tilde{\gamma}_m^{m'} \approx \frac{w_0 v s^2}{\pi\hbar^4 c^3}\frac{(E_m - E_{m'})^3}{1 - \exp[-\beta(E_m - E_{m'})]}$$

$$\frac{\tilde{\gamma}_m^{m'}}{\gamma_m^{m'}} = \frac{w_0}{|\tilde{D}|s^2}\frac{\rho v c_s^2}{|\tilde{D}|}\frac{c_s^3}{c^3}$$



Temperature dependence of the relaxation time τ in Fe8