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Phase Transition of the Escape Rate in Large Spin Dimer Model

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Outline

Model Hamiltonian

$$\hat{H} = J\hat{\mathbf{S}}_A \cdot \hat{\mathbf{S}}_B - D\left(\hat{S}_{A,z}^2 + \hat{S}_{B,z}^2\right) + h_z(\hat{S}_{A,z} - \hat{S}_{B,z})$$

- $J > 0$ is the antiferromagnetic interaction, $D > 0$ is an easy-axis anisotropy, and $h_z = g\mu_B h$ is the external staggered magnetic field.
- We consider the case of strong anisotropy $D \gg J$
- We also consider the case of equal spins $s_A = s_B = s$. For $[Mn_4O_3Cl_4(O_2CEt)_3(py)_3]_2$ or $[Mn_4]_2$ dimer $s = \frac{9}{2}$ (exact numerical diagonalization) *Wernsdorfer W. et al, PRL 91, 227203 (2003)*
- We will specialize on large spins $s \gg 1$

Outline

Spin wave function

- Consider the problem of finding the exact eigenvalues of the system for large spins $s \gg 1$:
- The spin wavefunction in the Hilbert space dim($\mathcal{H}$) = dim($\mathcal{H}_A \otimes \mathcal{H}_B$)= $(2s_A+1)\otimes(2s_B+1)$ can be written as:

$$\psi = \psi_A \otimes \psi_B = \sum_{\substack{m_A=-s_A\\ m_B=-s_B}}^{s_A,s_B} \mathcal{C}_{m_A,-m_B}\mathcal{M}_{m_A,-m_B}$$

where

$$\mathcal{M}_{m_A,-m_B} = \binom{2s_A}{s_A+m_A}^{-1/2}\binom{2s_B}{s_B-m_B}^{-1/2} \mid m_A,-m_B\rangle$$

Eigenvalue equation

$$\hat{H}\psi = \mathcal{E}\psi$$

$$\mathcal{E}\mathcal{C}_{m_A,-m_B} = \left[-Jm_Am_B - D(m_A^2 + m_B^2) + h_z(m_A + m_B)\right]\mathcal{C}_{m_A,-m_B} + \frac{J(s_A - m_A + 1)(s_B - m_B + 1)}{2}\mathcal{C}_{m_A-1,-m_B+1} + \frac{J(s_A + m_A + 1)(s_B + m_B + 1)}{2}\mathcal{C}_{m_A+1,-m_B-1}$$

Exact solution for $\mathcal{E}$ exits for small spins: 1/2,1,3/2,2.

What about large spins, say $s = 20, 50, 100$?

Generating function

$$\mathcal{F}(x_1, x_2) = \sum_{\substack{m_A=-s_A \\ m_B=-s_B}}^{s_A, s_B} \mathcal{C}_{m_A,-m_B} e^{m_A x_1} e^{-m_B x_2}$$

Eigenvalue equation becomes:

$$-D\left(\frac{d^2\mathcal{F}}{dx_1^2} + \frac{d^2\mathcal{F}}{dx_2^2}\right) - J\cosh(x_1 - x_2)\frac{d}{dx_1}\left(\frac{d\mathcal{F}}{dx_2}\right)$$
$$+J\frac{d}{dx_1}\left(\frac{d\mathcal{F}}{dx_2}\right) - (h_z - Js_A\sinh(x_1 - x_2))\frac{d\mathcal{F}}{dx_2}$$
$$+(h_z - Js_B\sinh(x_1 - x_2))\frac{d\mathcal{F}}{dx_1} + (Js_As_B\cosh(x_1 - x_2) - \mathcal{E})\mathcal{F} = 0$$

Differential equation with variable coefficients

$$r = x_1 - x_2, \quad q = \frac{x_1 + x_2}{2}$$

$$\mathcal{P}_1(r)\frac{d^2\mathcal{F}}{dr^2} + \mathcal{P}_2(r)\frac{d^2\mathcal{F}}{dq^2} + \mathcal{P}_3(r)\frac{d\mathcal{F}}{dr} + \mathcal{P}_4(r)\frac{d\mathcal{F}}{dq} + (\mathcal{P}_5(r) - \mathcal{E})\mathcal{F} = 0$$

$$\mathcal{P}_1(r) = -2\left[D + \frac{J}{2} - \frac{J}{2}\cosh r\right], \quad \mathcal{P}_2(r) = -\frac{1}{2}\left[D - \frac{J}{2} + \frac{J}{2}\cosh r\right]$$

$$\mathcal{P}_3(r) = (2g\mu_B h - J(s_A + s_B)\sinh r), \quad \mathcal{P}_4(r) = \frac{J(s_A - s_B)}{2}\sinh r,$$

$$\mathcal{P}_5(r) = J s_A s_B \cosh r$$

Couldn't find a solution of the ODE for $s_A \neq s_B$!!!.
For $s_A = s_B = s$, $\mathcal{P}_4(r) = 0$, solution exits: $\mathcal{F}(r, q) = \mathcal{X}(r)\mathcal{Y}(q)$

Differential equation for $s_A = s_B = s$

The generating function simplifies to:

$$\mathcal{F}(r,q) = \sum_{\substack{m_A=-s \\ m_B=-s}}^{s,s} \mathcal{C}_{m_A,-m_B} e^{\frac{(m_A+m_B)r}{2}} \underbrace{e^{\frac{(m_A-m_B)q}{2}}}_{1} = \mathcal{X}(r)$$

The ODE becomes ($r \to r + i\pi$ for convenience):

$$-2\left(D + \frac{J}{2} + \frac{J}{2}\cosh r\right)\frac{d^2\mathcal{X}}{dr^2} + 2(g\mu_B h + Js\sinh r)\frac{d\mathcal{X}}{dr}$$
$$-\left(Js^2\cosh r - \mathcal{E}\right)\mathcal{X} = 0$$

If we could eliminate the first derivative term, then the resulting equation is the well-known Schrödinger equation

Schrödinger equation

Introducing a particle wavefunction:

$$\Psi(r) = e^{-y(r)}\mathcal{X}(r), \quad \Psi(r) \to 0 \quad \text{as} \quad r \to \pm\infty$$

$$y(r) = s\ln[(2+\kappa+\kappa\cosh r)]\frac{2\tilde{s}\alpha}{\sqrt{1+\kappa}}\,\text{arctanh}\left[\frac{\tanh\left(\frac{r}{2}\right)}{\sqrt{1+\kappa}}\right]$$

where $\tilde{s} = (s+\frac{1}{2})$, $\kappa = J/D$ and $\alpha = h_z/2D\tilde{s}$.

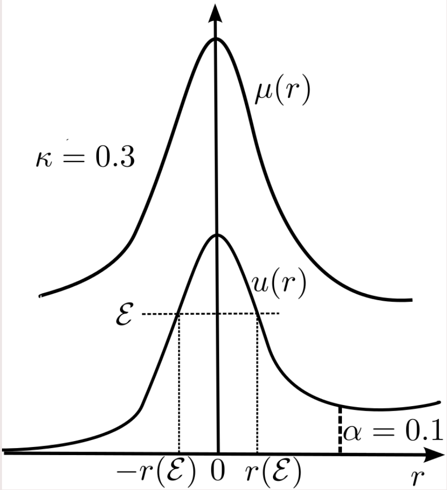
The ODE for $\Psi(r)$ becomes a Schrödinger equation:

$$H\Psi(r) = \mathcal{E}\Psi(r): \quad H = -\frac{1}{2\mu(r)}\frac{d^2}{dr^2} + U(r)$$

$$U(r) = 2D\tilde{s}^2 u(r), \quad u(r) = \frac{2\alpha^2 + \kappa(1-\cosh r) + 2\alpha\kappa\sinh r}{(2+\kappa+\kappa\cosh r)}$$

$$\mu(r) = [2D\,(2+\kappa+\kappa\cosh r)]^{-1}$$

Effective potential and reduced mass



Outline

Escape rate

The escape rate in the semiclassical approximation is given by (*Affleck PRL 46, 388, 1981*)

$$\Gamma \propto \int_{U_{\text{min}}}^{U_{\text{max}}} d\mathcal{E}\mathcal{P}(\mathcal{E})e^{-\beta(\mathcal{E}-U_{\text{min}})}, \quad \beta^{-1} = T$$

The transition amplitude and the Euclidean action are given by

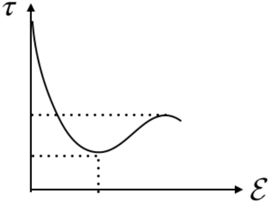
$$\mathcal{P}(\mathcal{E}) \sim e^{-S(\mathcal{E})}, \quad S(\mathcal{E}) = 2\int_{-r(\mathcal{E})}^{r(\mathcal{E})} dr\sqrt{2\mu(r)(U(r)-\mathcal{E})}$$

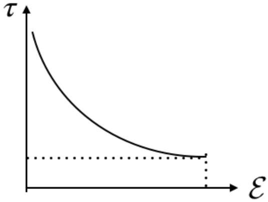
As $\beta \to \infty (T \to 0)$, which is related to $\hbar \to 0$ in Feynman path integral. The integral is dominated by the stationary point:

$$\beta = \tau(\mathcal{E}) = -\frac{dS(\mathcal{E})}{d\mathcal{E}} = \int_{-r(\mathcal{E})}^{r(\mathcal{E})} dr\sqrt{\frac{2\mu(r)}{U(r)-\mathcal{E}}}$$ period of oscillation

Escape rate

The order of phase transition can be characterized by the behaviour of $\tau(\mathcal{E})$ (*Chudnovsky PRA 46, 8011, (1992)*)





- If $\tau(\mathcal{E})$ is a nonmonotonic function of $\mathcal{E}$, in other words $\tau(\mathcal{E})$ has a minimum at some point $\mathcal{E}_1 < \Delta U$ (ΔU barrier height) and then rises again we get a first-order phase transition
- If $\tau(\mathcal{E})$ is monotonically increasing with decreasing $\mathcal{E}$ we get a second-order phase transition

Escape rate

The escape rate in this approximation can also be written as (*Chudnovsky and Garanin PRL 79, 4469, 1997*)

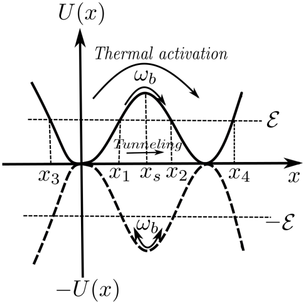
$$\Gamma \sim e^{-\beta F_{\text{min}}}$$

and F_{min} is the minimum of the effective free energy

$$F = \mathcal{E} + \beta^{-1} S(\mathcal{E}) - U_{\text{min}}$$

with respect to $\mathcal{E}$.
The order of phase transition can be also be analyzed with the free energy if the Euclidean action $S(\mathcal{E})$ can be calculated.

Escape rate



As $T \to 0$, $\mathcal{E} \to U_{\text{min}}$, the escape rate (tunneling rate) is

$\Gamma \propto e^{-B}$ B is the instanton action

As $T > \hbar\omega_0$, $\mathcal{E} \to U_{\text{max}}$ the particle can cross over the barrier (classical activation)

$\Gamma \propto e^{-\frac{\Delta U}{T}}$ ΔU barrier height

Crossover temperature from quantum to classical regimes
$T_0^{(1)} = \Delta U/B$ (First-order phase transition).
Comparing with the WKB exponent $e^{-\frac{2\pi\Delta U}{\omega_b}}$, $\omega_b^2 = -U''(x_s)/\mu(x_s)$ at $T = 0$:
$T_0^{(2)} = \omega_b/2\pi$ (Second-order phase transition)

Phase transition at zero field $\alpha = 0$ — Euclidean action

At zero magnetic field the effective potential reduces to:

$$U(r) = \frac{2D\kappa s^2(1-\cosh r)}{(2+\kappa+\kappa\cosh r)}$$

The exact Euclidean action is found to be:

$$S(\mathcal{E}) = 4s\sqrt{2(a+b)\kappa}[\mathcal{K}(\lambda') - (1-\gamma^2)\Pi(\gamma^2, \lambda')], \quad \lambda'^2 = \frac{a-b}{a+b}$$

where $a = 1-(2+\kappa)\mathcal{E}'$, $b = 1+\kappa\mathcal{E}'$, and $\mathcal{E}' = \mathcal{E}/2Ds^2\kappa$.
$\gamma^2 = \lambda'^2(1+\kappa)^{-1}$.
The functions $\mathcal{K}(\lambda')$ and $\Pi(\gamma^2, \lambda')$ are known as the complete elliptic integral of first and third kinds respectively.

Phase transition at zero field $\alpha = 0$ — Free energy

Introducing the dimensionless energy quantity:

$$Q = \frac{U_{\text{max}} - \mathcal{E}}{U_{\text{max}} - U_{\text{min}}}, \quad Q \to 0 \text{ as } \mathcal{E} \to U_{\text{max}} \text{ and } Q \to 1 \text{ as } \mathcal{E} \to U_{\text{min}}$$

Also a dimensionless temperature quantity: $\theta = T/T_0^{(2)}$

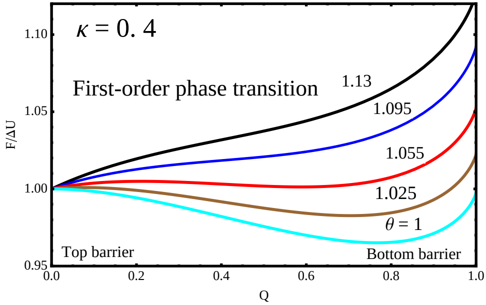
$$\lambda'^2 = \frac{(1+\kappa)Q}{\kappa + Q}, \quad \gamma^2 = \frac{Q}{\kappa + Q}$$

$$F/\Delta U = 1 - Q + \frac{4}{\pi}\theta\sqrt{\kappa(\kappa + Q)}[\mathcal{K}(\lambda') - (1-\gamma^2)\Pi(\gamma^2, \lambda')]$$

$$\tau(\mathcal{E}) = \frac{2}{Ds\sqrt{(\kappa + Q)}}\mathcal{K}(\lambda')$$

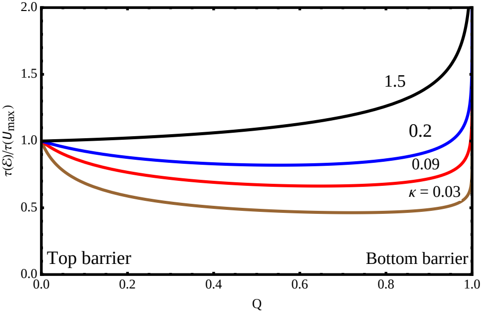
where $\Delta U = 2Ds^2$

Phase transition at zero field $\alpha = 0$ — Free energy



- The free energy for $\kappa = 0.4$ has one minimum at $\theta = 1.13$, as θ is decreased, there can be two or more minima. First-order phase transition occurs when the two minima are the same i.e $\theta = 1.055$ or $T_0^{(1)} = 1.055 T_0^{(2)}$ where $T_0^{(2)} = \frac{\omega_b}{2\pi} = \frac{Ds\sqrt{\kappa}}{\pi}$

Phase transition at $\alpha = 0$ — Period of oscillation



- For $\kappa > 1$, the period monotonically increases with decreases energy —Second-order transition
- For $\kappa < 1$, the period has a minimum and arises again —First-order transition

Phase transition at $\alpha = 0$ — Landau theory

Near the top of the barrier $Q \to 0$, the free energy simplifies:

$$F/\Delta U = 1+(\theta-1)Q+\frac{\theta}{8\kappa}(\kappa-1)Q^2+\frac{\theta}{64\kappa^2}(3\kappa^2-2\kappa+3)Q^3+O(Q^4)$$

The Landau's free energy has the form:

$$F = F_0 + a\psi^2 + b\psi^4 + c\psi^6$$

- The coeff. a is related to the coeff. of Q. It changes sign at $T = T_0^{(2)}$.
- The phase boundary between the first- and the second-order phase transitions depends on the coeff. b, which is related to the coeff. of Q^2. It changes sign at $\kappa = 1$. Thus $\kappa < 1$ indicates the first-order phase transition.

Phase transition at $\alpha \neq 0$ — Euclidean action

At non-zero field there is no exact expression for $S(\mathcal{E})$.
Expanding near the top of the barrier r_b (Kim, JAP 86, 1062, 1999.):

$$S(\mathcal{E}) = \pi\sqrt{\frac{2\mu(r_b)}{U''(r_b)}}\Delta U[Q + \mathcal{G}Q^2 + O(Q^3)]$$

$$\mathcal{G} = \frac{\Delta U}{16UU''}\left[\frac{12U''''U'' + 15(U''')^2}{2(U'')^2} + 3\left(\frac{\mu'}{\mu}\right)\left(\frac{U'''}{U''}\right) + \left(\frac{\mu''}{\mu}\right) - \frac{1}{2}\left(\frac{\mu'}{\mu}\right)^2\right]_{r=r_b}, \quad r_b = \ln\left(\frac{1+\alpha}{1-\alpha}\right), \quad \Delta U = 2D\tilde{s}^2(1-\alpha)^2$$

$U''(r_b) = -D\tilde{s}^2u''(r_b)/2!$, $U'''(r_b) = D\tilde{s}^2u'''(r_b)/3!$,
$U''''(r_b) = D\tilde{s}^2u''''(r_b)/4!$.

Phase transition at $\alpha \neq 0$ — Free energy

The free energy has the form:

$$F(Q)/\Delta U = 1 + (\theta - 1)Q + \theta \mathcal{G} Q^2 + \cdots$$

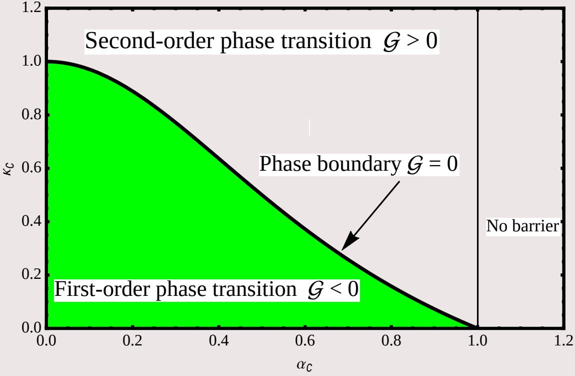
The Landau coefficient is found to be:

$$\mathcal{G} \equiv b = \frac{(\kappa - 1 + \alpha^2(1 + 2\kappa))}{8\kappa(1 + \alpha)^2}$$

- First-order transition $\mathcal{G} < 0$. Second-order transition $\mathcal{G} > 0$
- At the phase boundary $\mathcal{G} \equiv b = 0$ which yields

$$\alpha_c = \pm\sqrt{\frac{1 - \kappa_c}{1 + 2\kappa_c}}$$

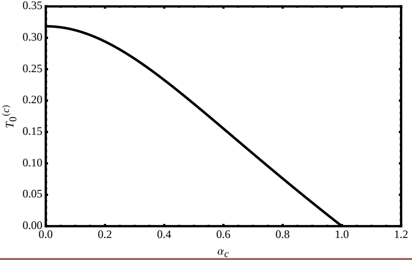
Phase transition at $\alpha \neq 0$ — Phase boundary



Phase transition at $\alpha \neq 0$ — Crossover temperature

The second-order crossover transition temperature at the phase boundary is given by

$$T_0^{(c)} = \frac{\omega_b^c}{2\pi} = \frac{D\tilde{s}}{\pi}\frac{(1-\alpha_c^2)}{\sqrt{1+2\alpha_c^2}} = \frac{D\tilde{s}\kappa_c}{\pi}\left(\frac{3}{1+2\kappa_c}\right)^{\frac{1}{2}}$$



- For $[Mn_4]_2$ dimer, the parameters are: $s = 9/2$, $D = 0.75K$, $J = 0.12K$.
- We obtain $T_0^{(c)} = 0.29K$. Smaller than Fe_8 molecular cluster $T_0^{(c)} = 0.79K$.

Outline

Conclusion

In conclusion:

- We have investigated an effective Hamiltonian of a dimeric molecular nanomagnet which interacts antiferromagnetically in a staggered magnetic field.
- We showed that the boundary between the first-and second-order phase transitions is greatly influenced by the staggered magnetic field.
- We obtained the crossover temperature at the phase boundary for $[Mn_4]_2$
- The results for the crossover temperatures can be investigated experimentally

THANK YOU