Calculation of the free energy of $NiFe_2O_4$ nanoparticles by Monte Carlo simulations

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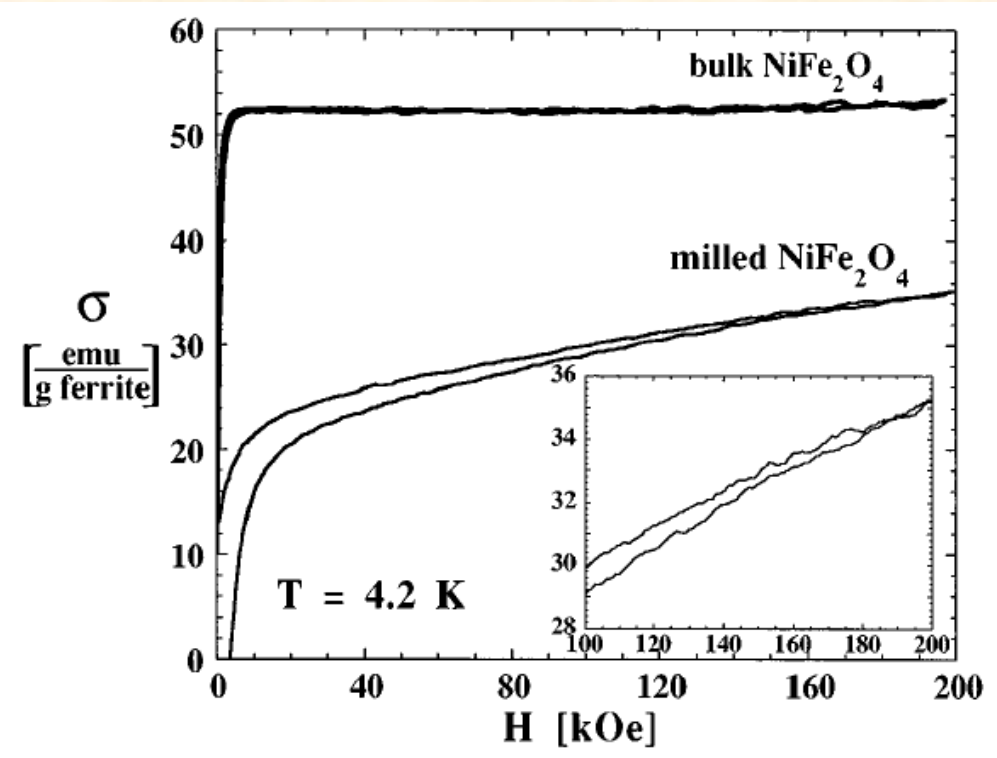
Introduction



ZFC magnetization hysteresis loops at 4.2K for bulk and milled (6.5nm) samples. From Kodama et. al. P. R. L. 77 394 (1996)

- Ferrimagnetic order in bulk material.
- $T_c = 838$ K
- Milled nanoparticles of size 1~10 nm.
- Reduced magnetic moment in low temperatures.
- Hysteresis loop opens up to 50 K.

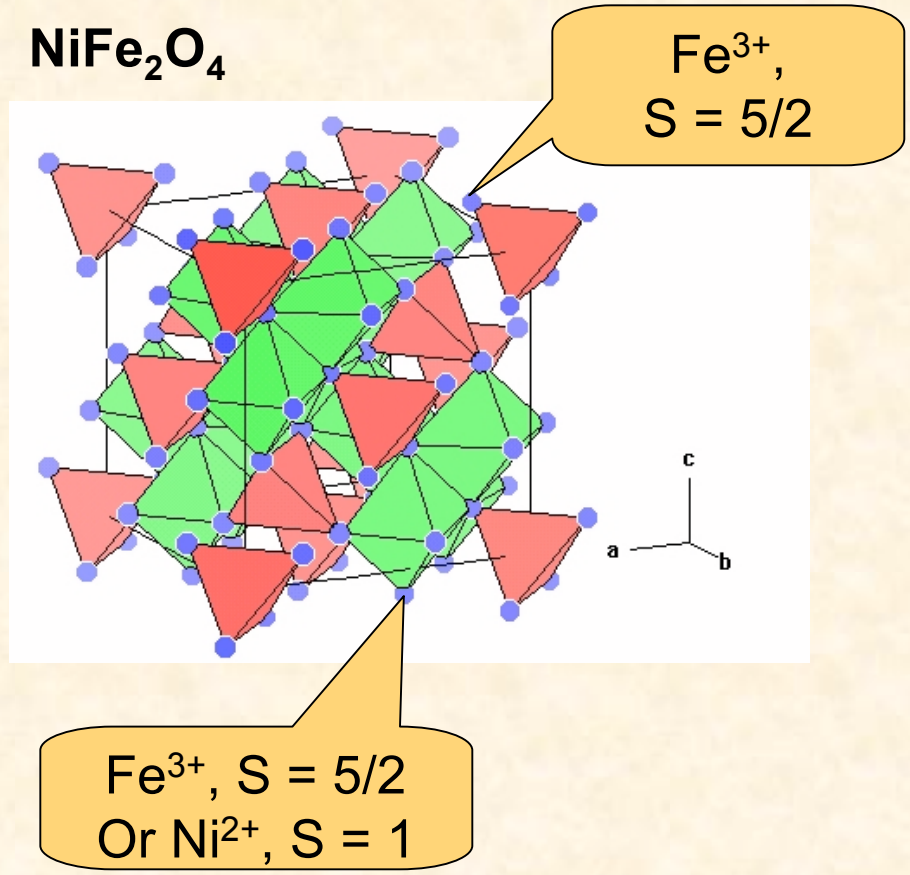
Crystal structure and Hamiltonian

- **Inverse spinel structure, Fe^{3+} occupy both half octahedral sites and all tetrahedral sites.**
- **Assume Fe and Ni have Verwey order.**

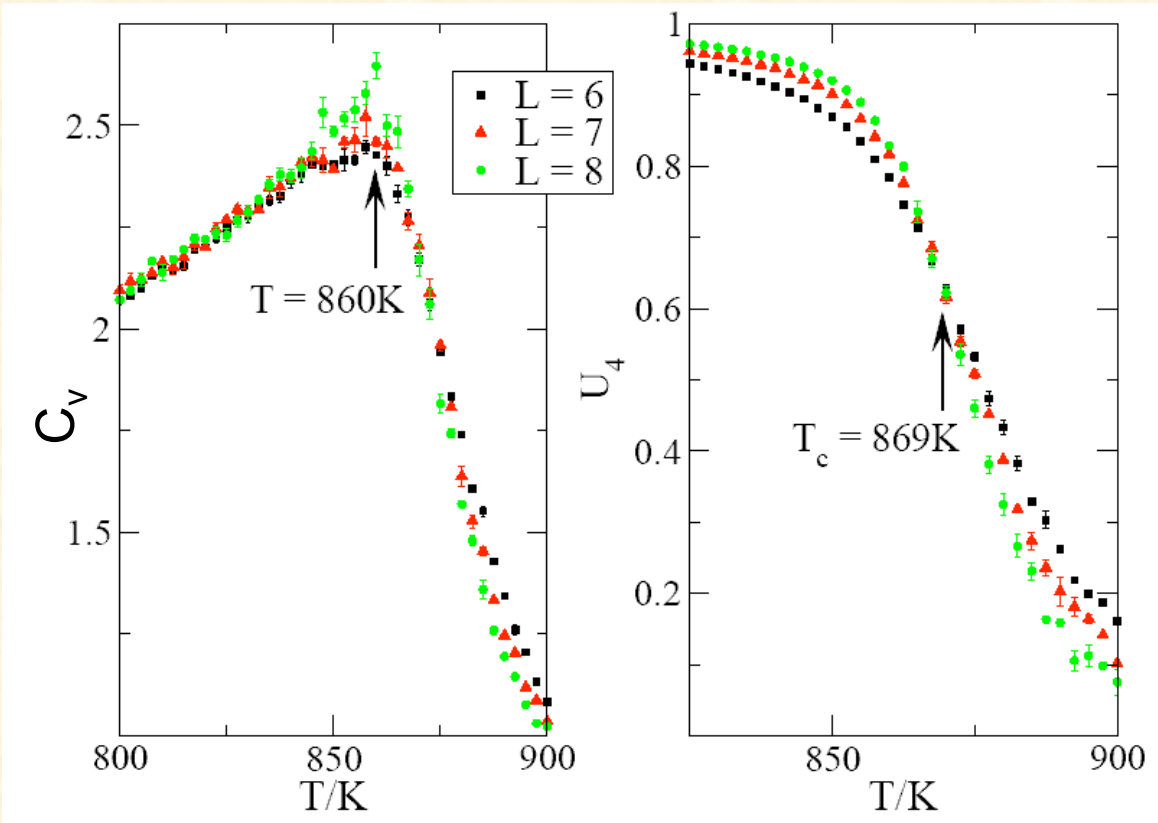
$$H = -\sum_{<i,j>} J_{ij} \mathbf{S}_i \cdot \mathbf{S}_j - \mathbf{h} \cdot \sum_i \mathbf{S}_i$$

- S_i **Classical Heisenberg spins of length 5/2 or 1.**
- J_{ij} **exchange constants.**

$NiFe_2O_4$



Bulk material



$-J_{ij}/K$	*A*	*B*	*B'*
A	*21*	*36*	*28.1*
B	*36*	*22*	*-2*
B'	*28.1*	*-2*	*8.6*

A: Fe on tetrahedral sites

B: Ni on octahedral

B': Fe on octahedral

Experimental value: T_c = 838 K

Surface disorder and anisotropy of nanoparticles

- **Surface disorder:** [Kodama et. al. P. R. L. 77 394 (1996)]
  - **Caused by missing Oxygen bonds and pinned spins.**
  - **Removing 15% surface spins randomly.**
- **Surface anisotropy:**
  - **Strong uniaxial anisotropy:**
  - **vector $\mathbf{n}$ is roughly normal to the surface.**

$$U = -k_s \left(\mathbf{S}_i \cdot \mathbf{n}_i\right)^2 S_i^{-2}$$

$$\mathbf{n}_i \propto \sum_j \left(\mathbf{r}_i - \mathbf{r}_j\right)$$

- **No quantitative theory is available.**

Joint density of states and free energy (H32.3)

- **Joint density of states:**

$$g(M,E)=\int \delta(E-E(S))\delta(M-M(S))\prod_i dS_i$$

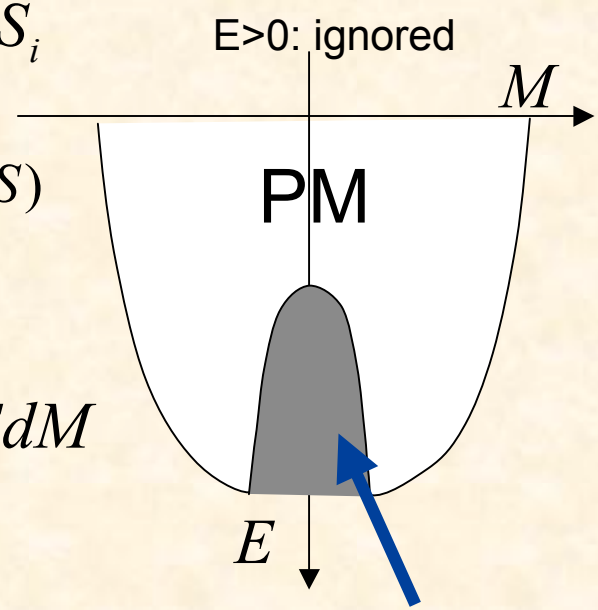
$$S=\{S_1,\ldots S_N\},\quad M(S)=\frac{1}{N}\left|\sum_i \mathbf{S}_i\right|,\quad E(S)=\frac{1}{N}H(S)$$

- **Free energy**

$$F(h,T)=-T\ln\int g(M,E)e^{-N(E-hM)/T}dEdM$$

- **Bragg-Williams Free energy**

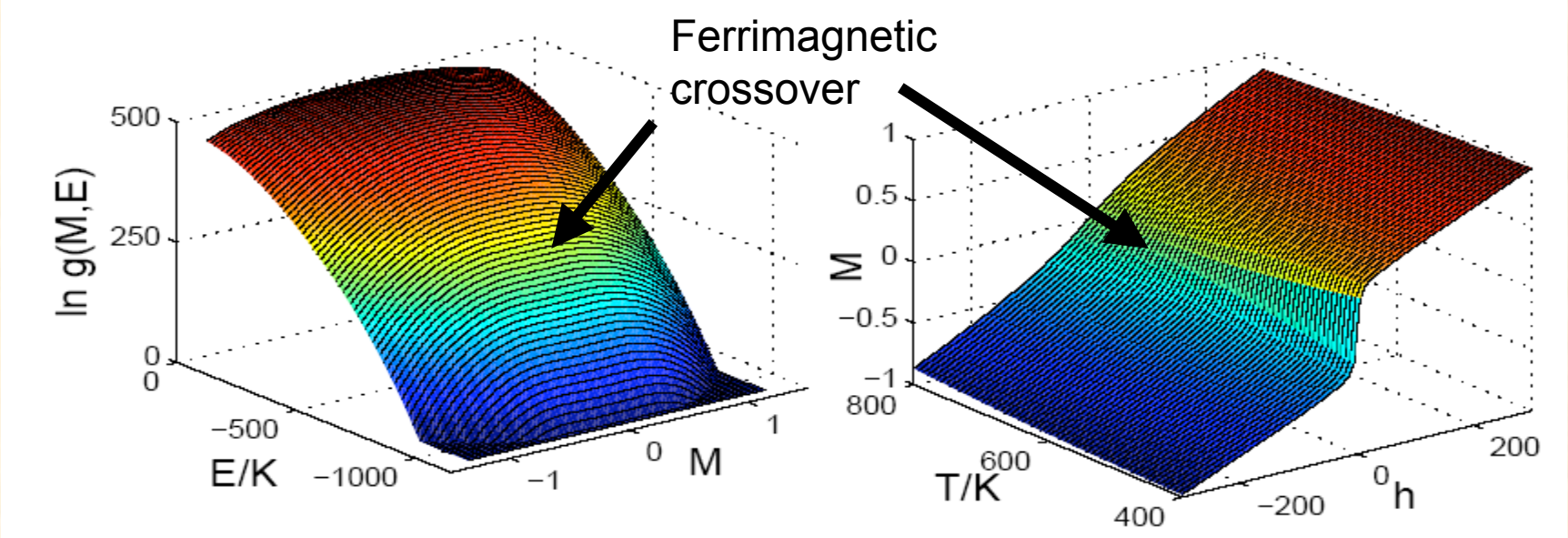
$$F(M,T)=-T\ln\int g(M,E)e^{-NE/T}dE$$



Ferrimagnetic :

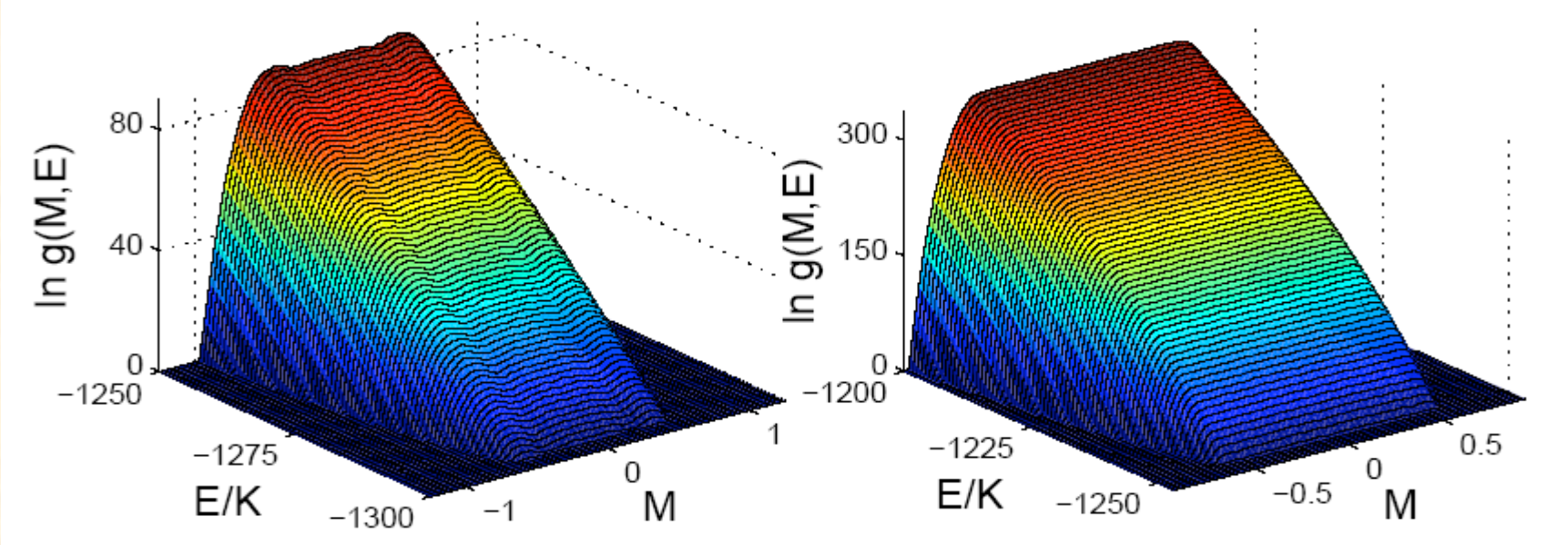
$$\partial \ln g/\partial M=0$$

Paramagnetic phase and the ferrimagnetic crossover regime



- A nanoparticle of 387 spins, 2.6nm in diameter
- A flat ($\partial \ln g / \partial M = 0$) area appears below a crossover energy.
- Indicating ferrimagnetic order and spontaneous magnetization.
- Crossover temperature ~ 650K < T_c of bulk material.

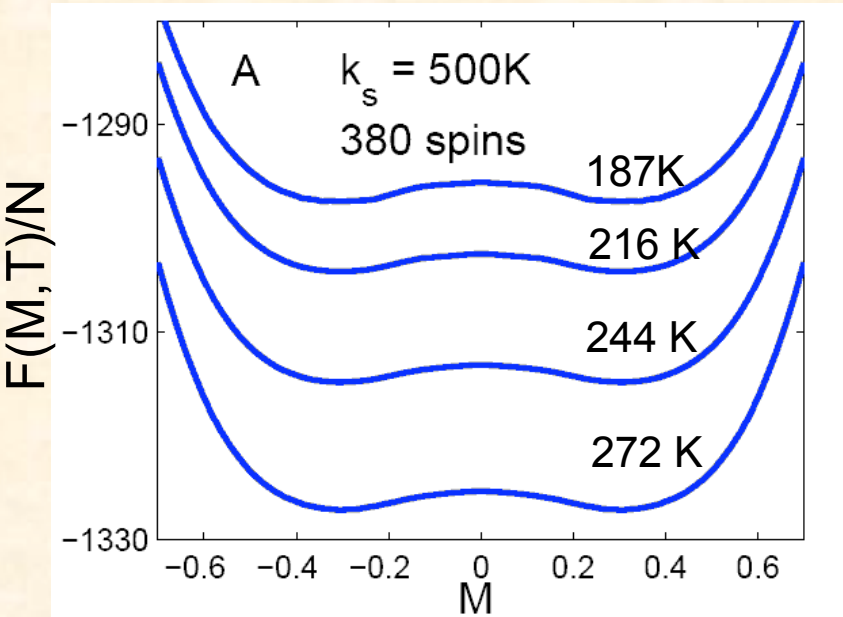
Ferrimagnetic phase

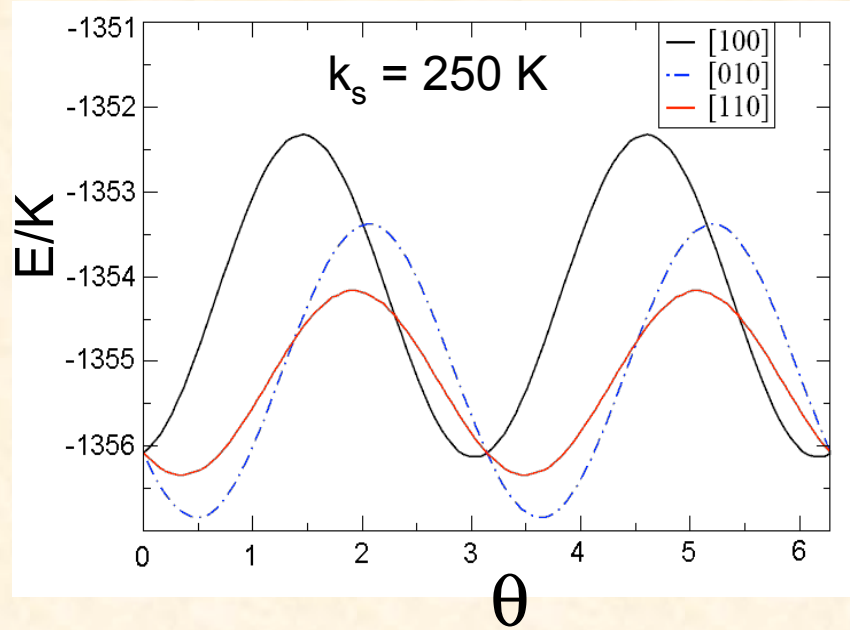


- k_s = 500K , 387 spins, with surface disorder.
- 180K < T < 250 K
- Valleys along constant magnetization appear, leading to meta-stable states and coercivity.

- Same nanoparticle, $k_s = 0$
- Rotational symmetry is intact.
- 30K < T < 100 K
- Flat density of states: superparamagnetism

Translated into Free energy





- Free energy barrier separates spontaneous magnetization.
- Leading to magnetic hysteresis.
- No hysteresis, if either surface disorder or anisotropy is absent.

- Energy of ferrimagnetic configuration as a function of rotation around different axes.
- Amplitude is comparable with free energy barrier.

Conclusions

- Nanoparticles show a smooth crossover to ferrimagnetic state.
- Reduced transition temperature and magentization.
- Strong surface anisotropy and disorder are necessary to induce free energy barrier and magnetic hysteresis.
- Otherwise, superparamagnetism is observed.

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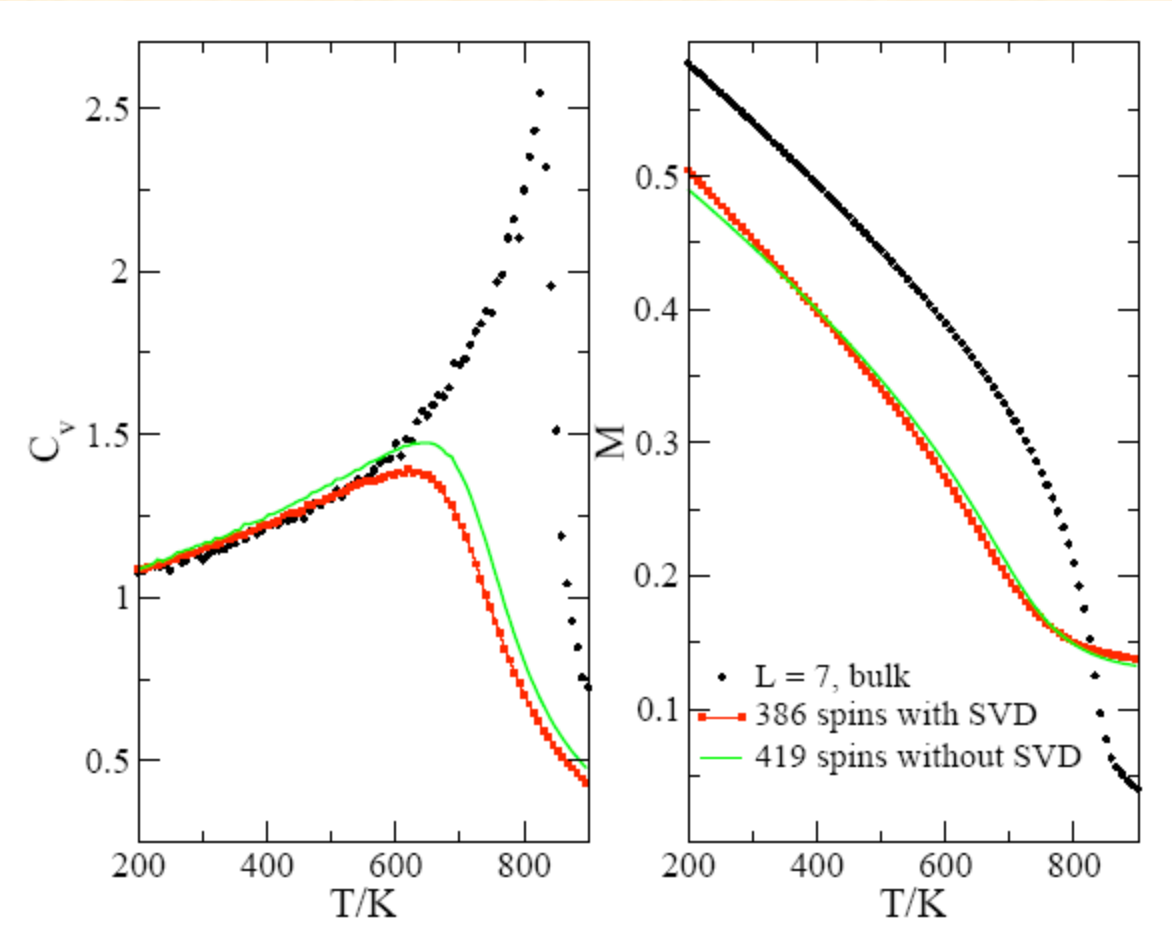
Nanoparticle in zero field



$$M = \frac{1}{N}\left|\sum_i \mathbf{S}_i\right|$$