Rate-dependent hysteresis in ensembles of magnetic nanoparticle clusters

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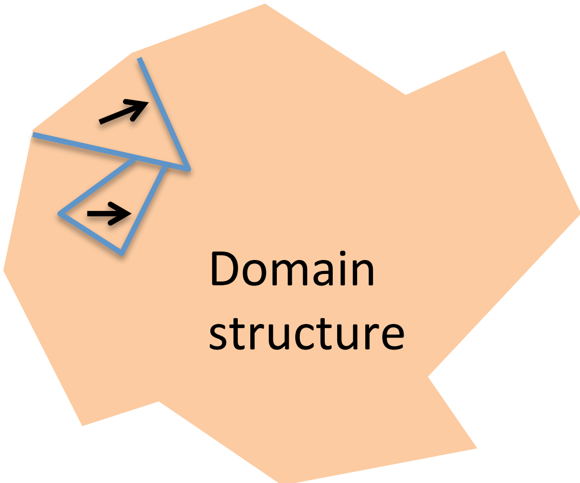
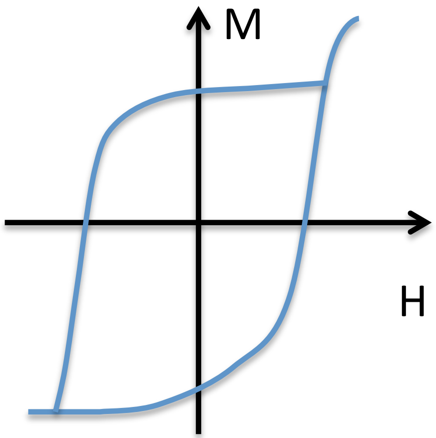
Outline

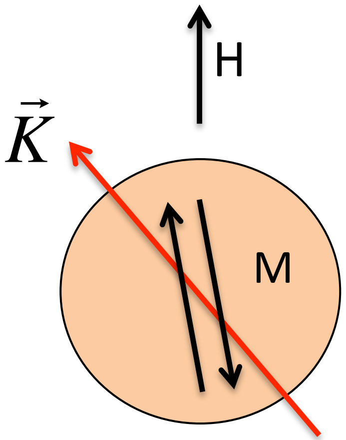
- Motivation: use of magnetic nanoparticles for:
  - Biological sensing + hyperthermia (heat assisted cancer treatment)
  - Optimization of thermal relaxation characteristics
  - Examples of study systems: single domain magnetic nanoparticles, chains, clusters
- Modeling:
  - Stoner-Wohlfarth particle model
  - Master equation + kinetic Monte-Carlo algorithm
- Thermal relaxation of magnetization
- Rate-dependence of hysteresis loops

Magnetism of nanoparticles





Domain has a critical size



Sub-domain size

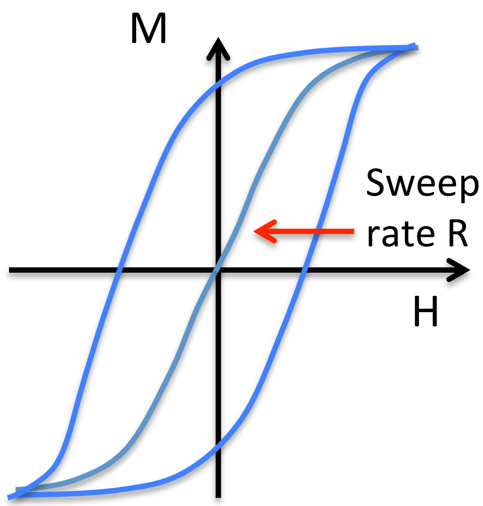
Ferromagnetism

- Stable moment M
- Hysteresis loop determined by K

Superparamagnetism

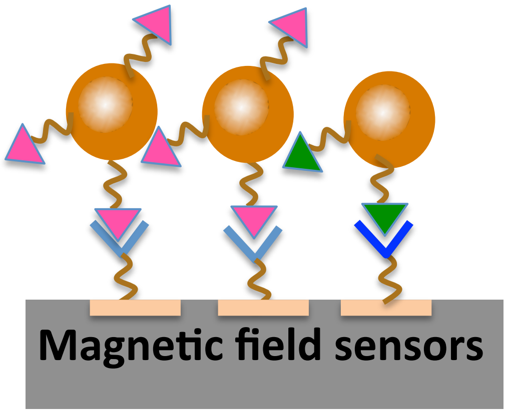
- Fluctuating moment M

$$\tau = \tau_0 \exp\left(-\frac{KV}{k_B T}\right)$$

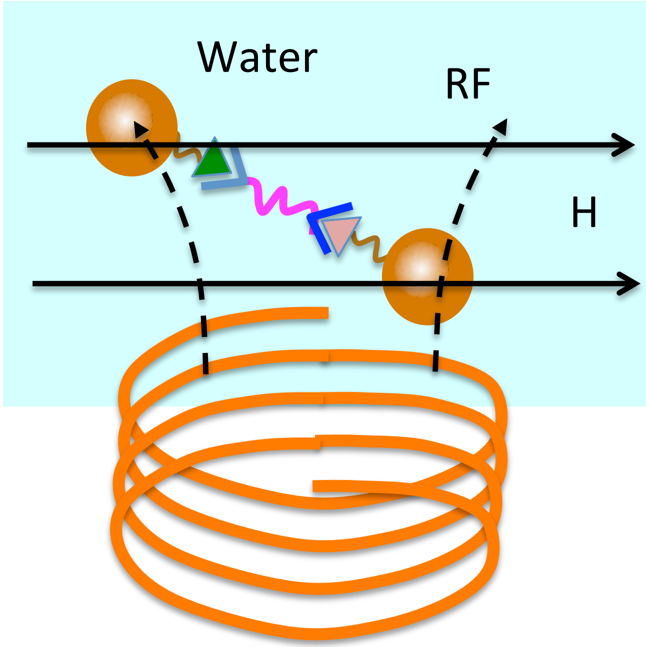


Rate-dependent hysteresis

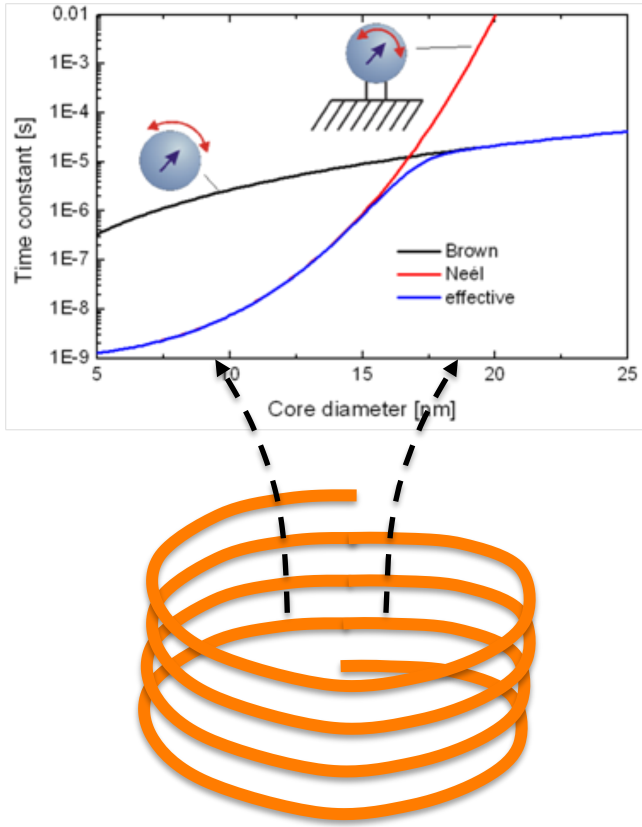
Magnetic Sensing



Superparamagnetic nanoparticles (and their aggregates) used to sense conjugation to surfaces. Multiplexing is possible based on position encoding, but only applicable near surfaces.

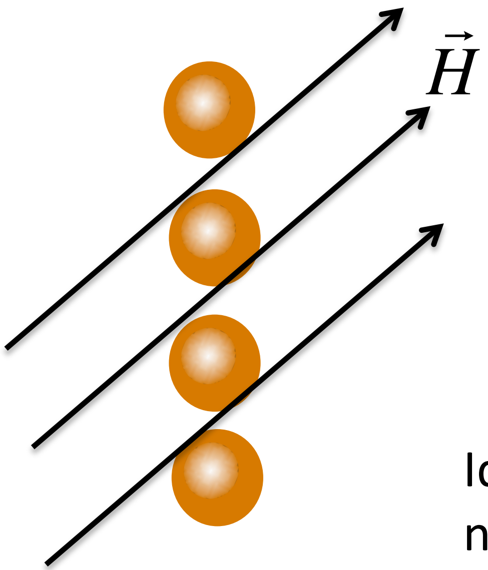


Magnetic resonance based detection (change in T2 relaxation of water) of the particle clustering due to specific interactions. Bulk measurement, but no multiplexing and weak sensitivity.



Sensing of particle magnetization relaxation by coils or SQUIDS. Bound/ unbound distinguished by relaxation time. Bulk measurement, but no multiplexing.

Can we manipulate Neel relaxation for the purposes of creating multiplexed separation and detection?

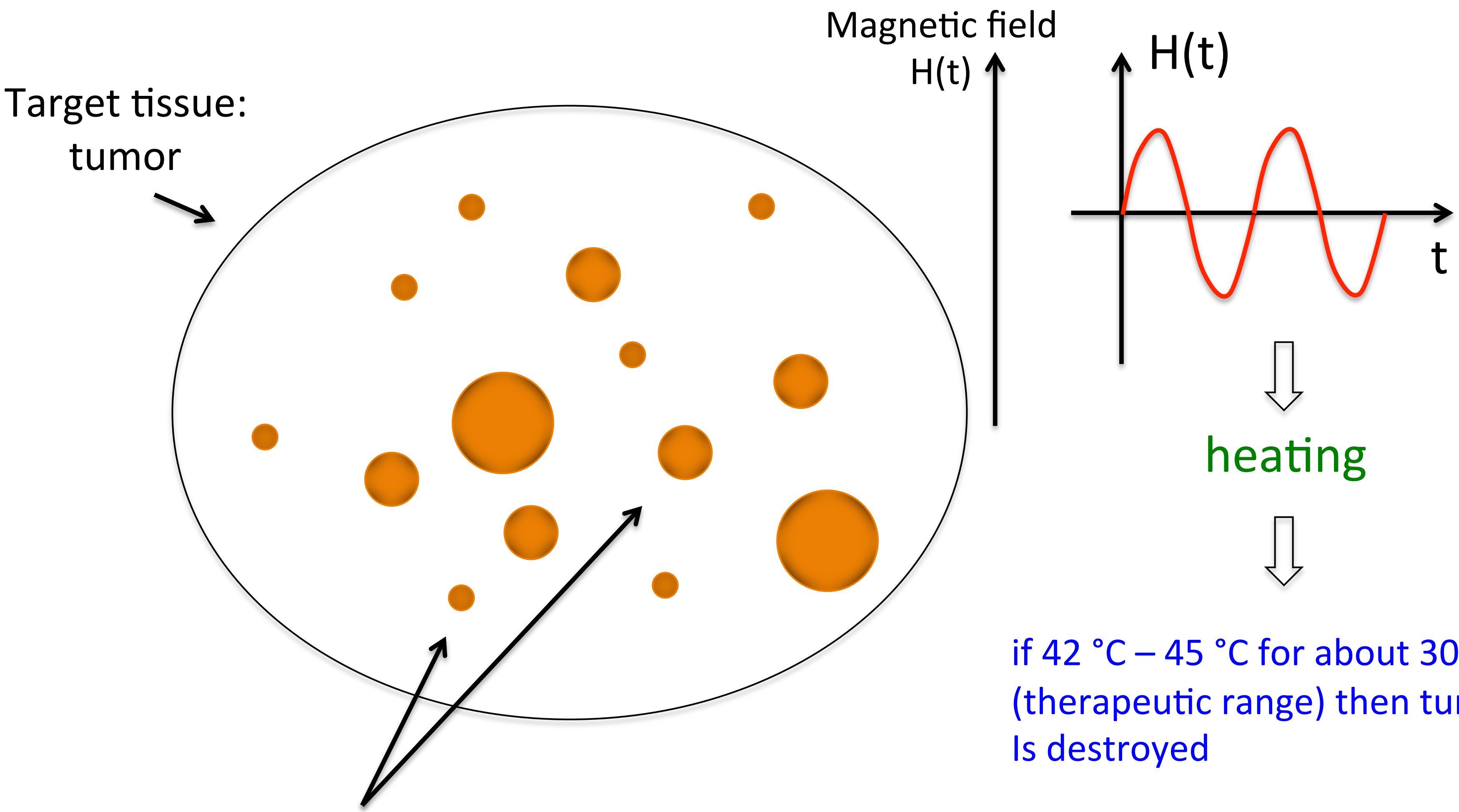


$$\tau = \tau_0 \exp\left(-\frac{V\left(\left(\vec{K}_i \cdot \hat{M}\right)^2 + \mu_0 M_S \hat{M} \cdot \vec{H}_{local}\right)}{k_B T} \right)$$

Idea: perhaps chains or fibers made of superparamagnetic nanoparticles can be good objects where Neel relaxation can be manipulated? Chains with different relaxation can be used as color in fluorescent detection.

- Relaxation can depend on relative orientation of chain axis and crystalline anisotropy axis
- Relative external field orientation
- Confounding factors: variation of size, anisotropy, inter-particle distance

Hyperthermia – cancer treatment using magnetic nanoparticles in time-varying magnetic field:



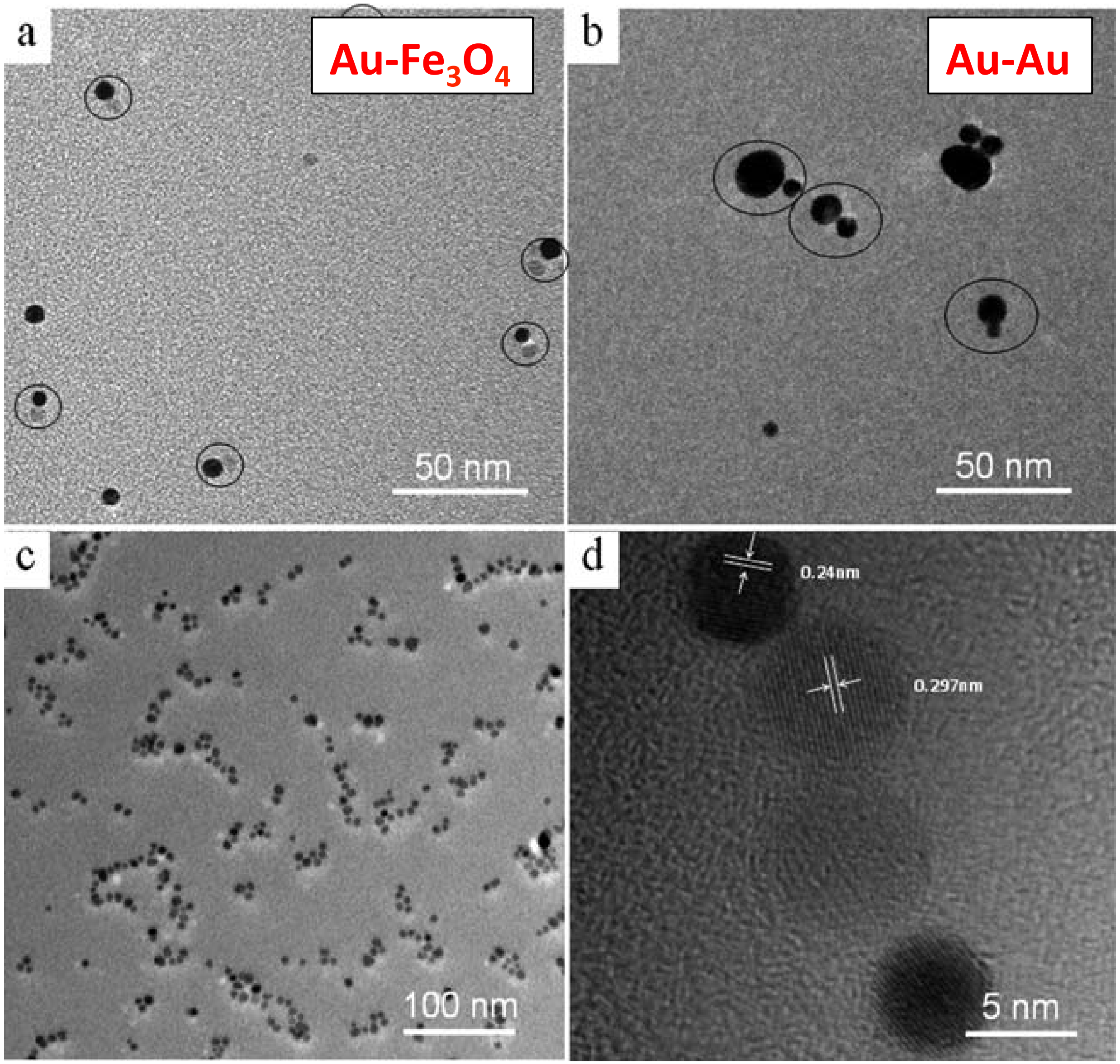
if 42 °C – 45 °C for about 30min (therapeutic range) then tumor Is destroyed

magnetic particles (variation in size, material properties, etc.)

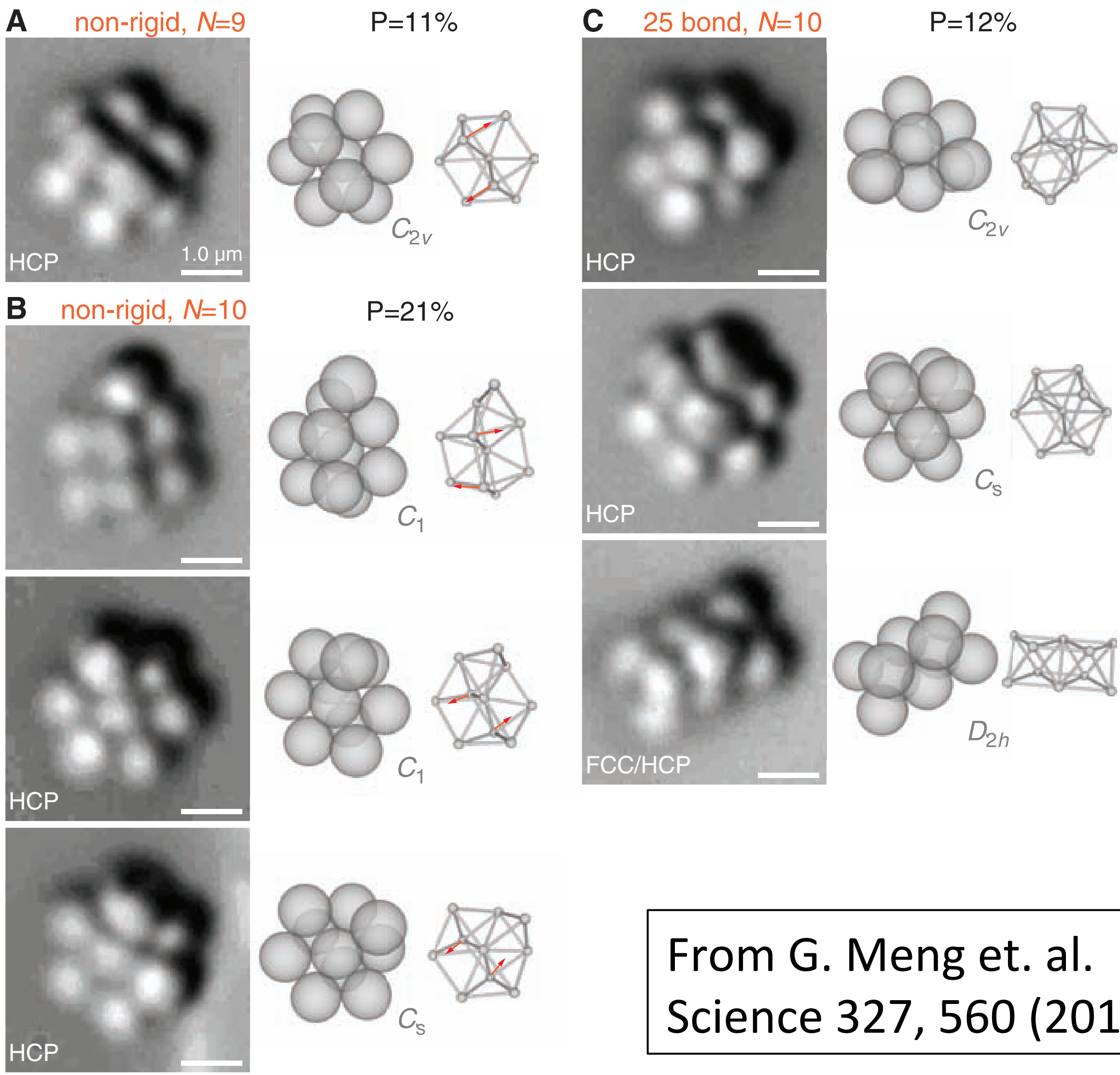
Q. A. Pankhurst et. al., J. Phys. D: Appl. Phys. 36, R167-R181 (2003)

Nanoparticle chains - design:

Bin Dong, Bing Li, Christopher Li,
J. Mater. Chem. 21, 13155 (2011)



Examples of clusters (aggregation+selection)



From G. Meng et. al.
Science 327, 560 (2010)

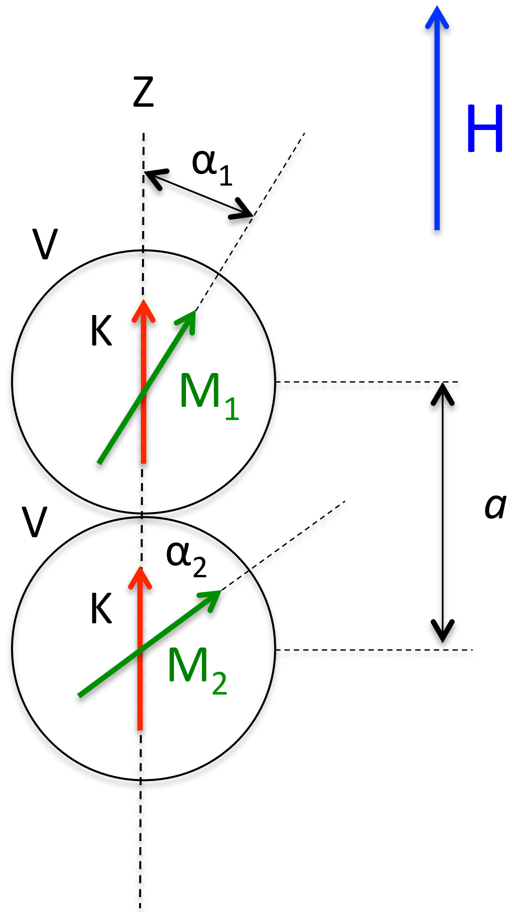
Stoner-Wohlfarth particles:

- Energy terms involved:

Anisotropy Energy | Zeeman Energy

$$e_{S,i} = -\frac{1}{2}\left(\hat{K}_i \cdot \hat{M}_i\right)^2 - h_i \hat{M}_i \cdot \hat{z} \quad \rightarrow \quad i = 1, \ldots, N$$

$$h_i = H / H_{K,i} \qquad H_{K,i} = 2K_i / \mu_0 M_S$$



- Dipolar interaction between the particles:

$$e_{dd} = I_{ij}\left[\hat{M}_i \cdot \hat{M}_j - 3\left(\hat{M}_i \cdot \hat{a}\right)\left(\hat{M}_j \cdot \hat{a}\right)\right] \qquad I_{ij} = \frac{V_j M_S}{4\pi a^3 H_{K,i}}$$

Thermal relaxation: Master-equation approach (symbolic):

$$\frac{d}{dt}P(\sigma_1,\sigma_2,\ldots,\sigma_N;t) = -\sum_{i=1}^{N} w_{i+/-}(\sigma_i)P(\sigma_1,\sigma_2,\ldots,\sigma_N;t)$$

$$+\sum_{i=1}^{N} w_{i-/+}(-\sigma_i)P(\sigma_1,\sigma_2,\ldots,-\sigma_i,\ldots,\sigma_N;t)$$

Relaxation rates (Arrhenius):

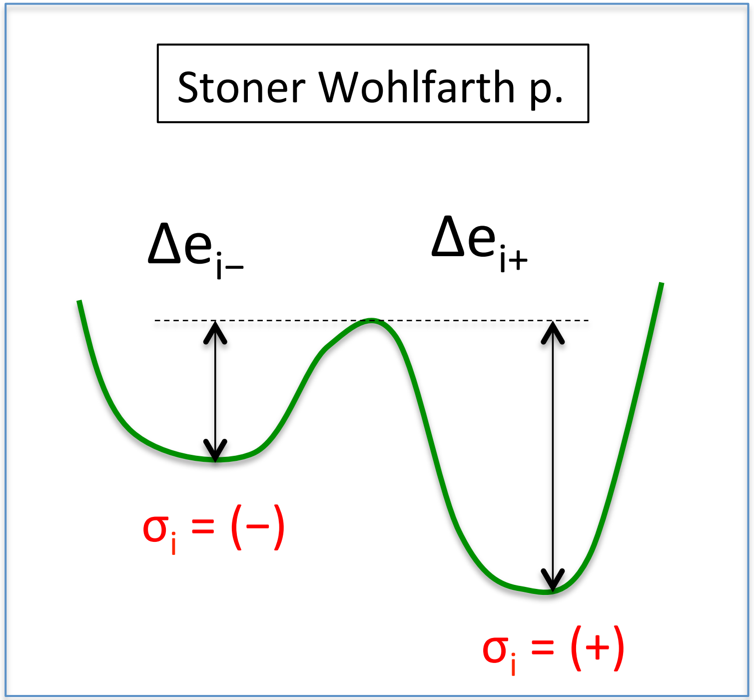
$$w_{i+} = f_0 \exp\left(-\Delta e_{i+}/k_B T\right)$$

$$w_{i-} = f_0 \exp\left(-\Delta e_{i-}/k_B T\right)$$

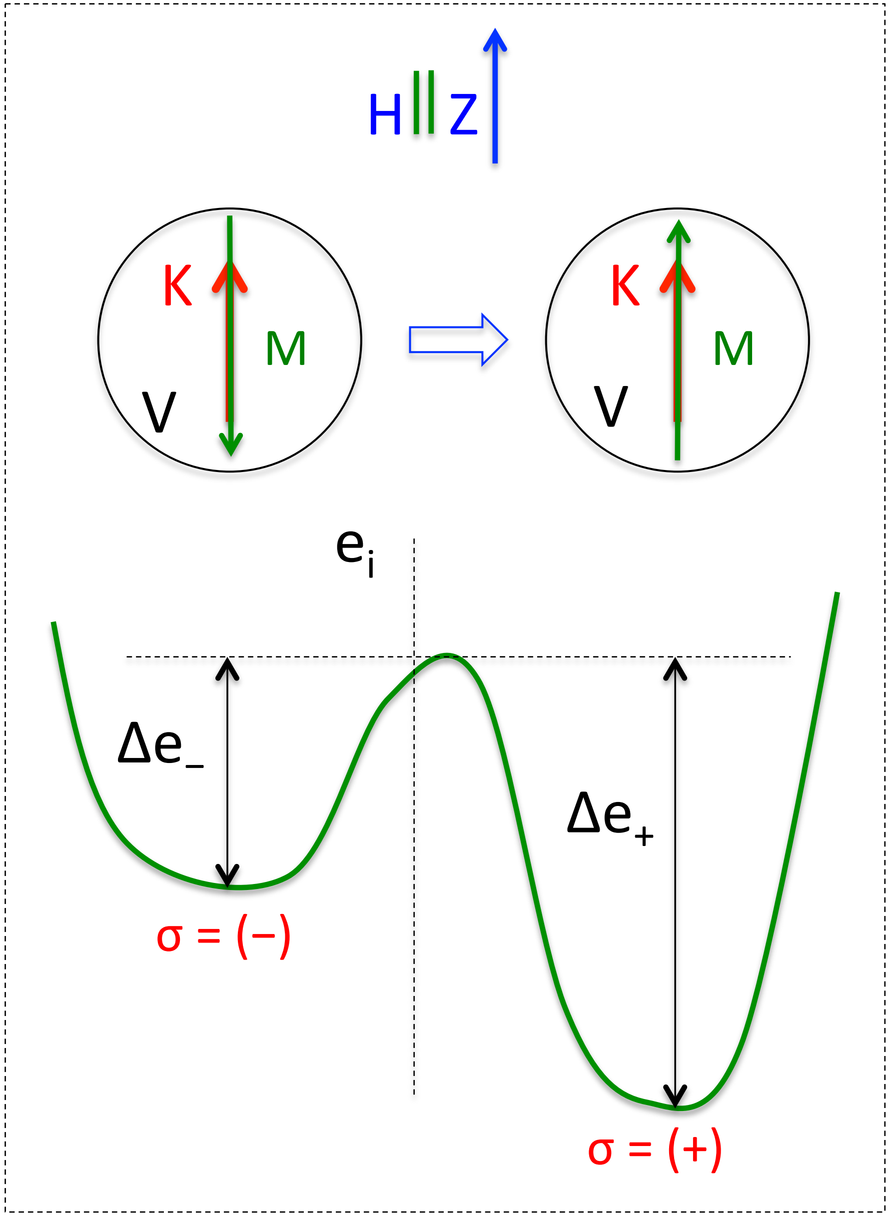
$$w_i = w_{i+} + w_{i-}$$

Initial condition (saturation):

$$P(\sigma_1,\sigma_2,\ldots,\sigma_N;t_0)$$



Example I: non-interacting (single particle) case:



- **Energy**

$$e = -\frac{1}{2}\left(\hat{K}\cdot\hat{M}\right)^2 - h\,\hat{M}\cdot\hat{z}$$

- **Find extrema, calculate En. barriers**

$$\Delta e_{\pm} = 2^{-1}\left(1 \pm h\right)^2$$

- **Relaxation rates (Arrhenius)**

$$w_{\pm} = f_0 \exp\left(-\frac{KV}{2k_B T}\left(1 \pm h\right)^2\right)$$

- **Master Equation:**

$$\begin{bmatrix} \dot{p}_+ \\ \dot{p}_- \end{bmatrix} = \begin{bmatrix} -w_+ & +w_- \\ +w_+ & -w_- \end{bmatrix} \begin{bmatrix} p_+ \\ p_- \end{bmatrix}$$

Example I: non-interacting (single particle) case:

- **Master Equation: Solution at constant H and T**

$$p_{\pm}(t) = p_{EQ}^{\pm}\left(1-\exp\left(-\frac{t}{\tau}\right)\right) + p_{\pm}(0)\exp\left(-\frac{t}{\tau}\right)$$

$$p_{EQ}^{\pm} = \frac{w_{\mp}}{w_{+}+w_{-}}$$

Equilibrium

$$\tau = \frac{1}{w_{+}+w_{-}}$$

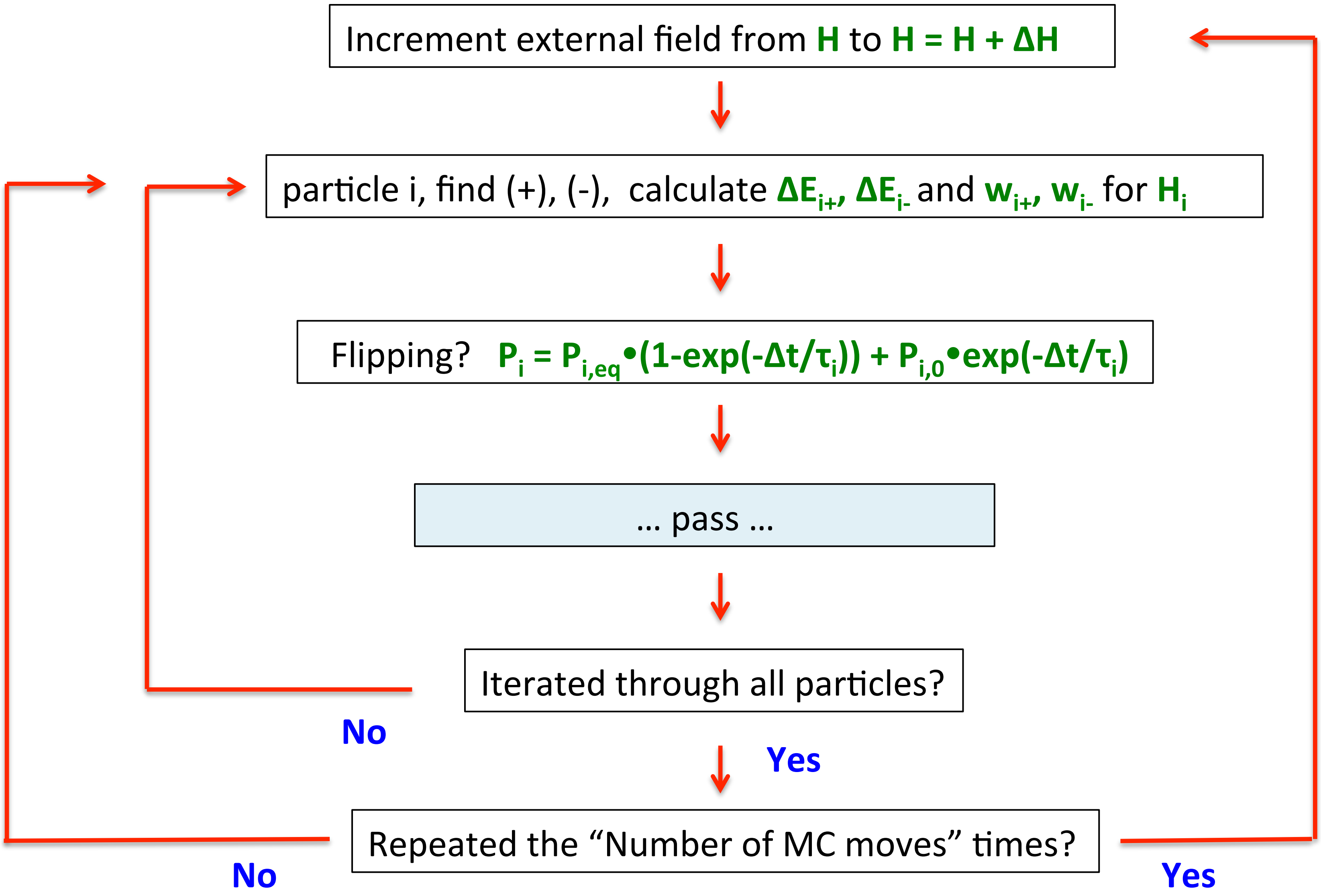
Relaxation time

Initial condition

- **Master Equation: time dependent H – increment H + ΔH in time steps Δt, starting from very large negative H when $p_{+}(0) = 0$**

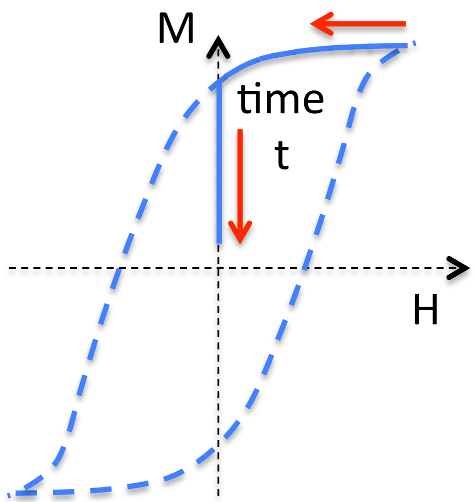
$$p_{-}(t_k) = \exp\left(-\Delta t \sum_{k=1}^{K} \frac{1}{\tau(t_k)}\right) \longrightarrow M(t_k)/M_S = 1 - 2p_{-}(t_k)$$

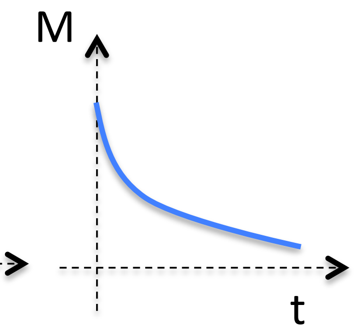
How we compute hysteresis loops: iterative solution of the master equation



Modeling two kinds of experiments:

- Magnetic relaxation: Set large magnetic field H, then instantaneously reduce H to 0 and let magnetization M evolve

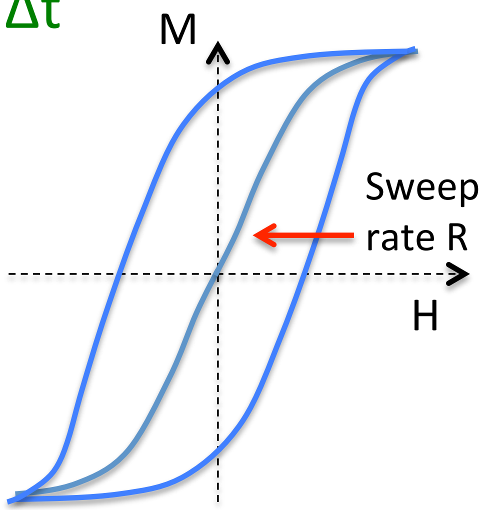




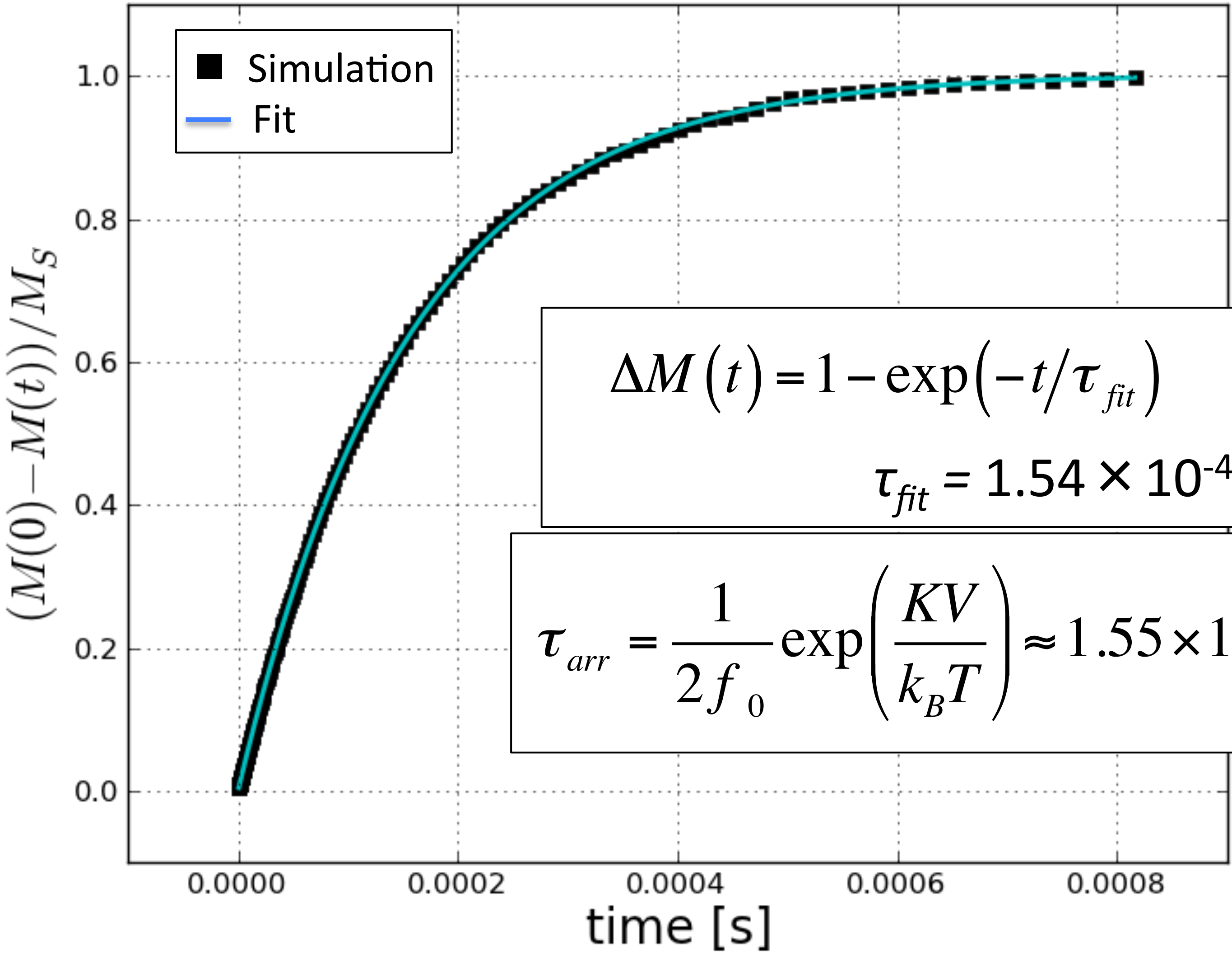
- Rate-dependent hysteresis loop: rate R = ΔH/Δt

$$M(t_k)/M_S = 1 - 2\exp\left(-\Delta t \sum_{k=1}^{K} \frac{1}{\tau(t_k)}\right)$$

$$= 1 - 2\exp\left(-\frac{1}{R} \sum_{k=1}^{K} \frac{\Delta H}{\tau(t_k)}\right)$$



Relaxation time: non-interacting case



$$\Delta M(t) = 1 - \exp\left(-t/\tau_{fit}\right)$$

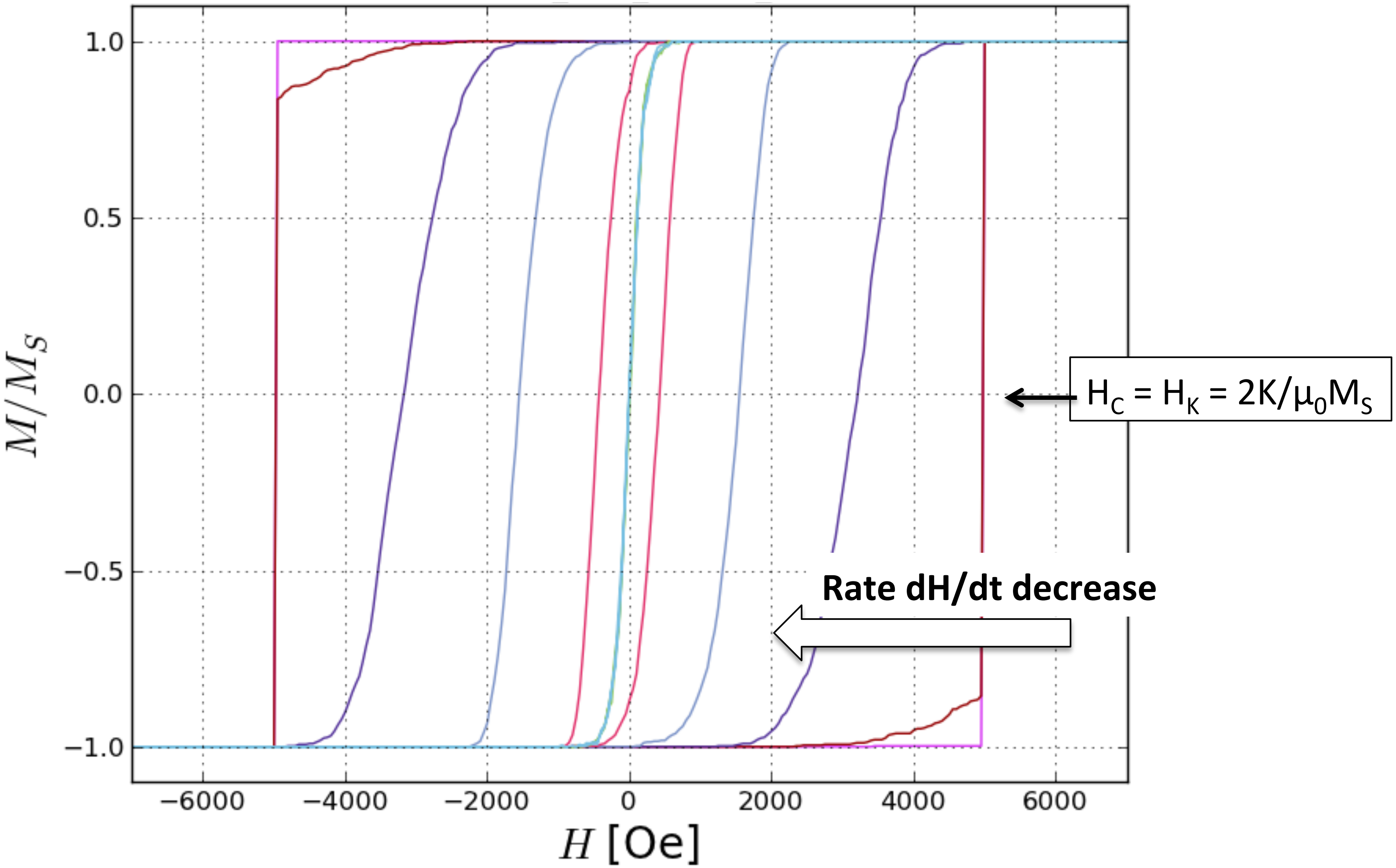
$$\tau_{fit} = 1.54 \times 10^{-4}\ s$$

$$\tau_{arr} = \frac{1}{2 f_0} \exp\left(\frac{KV}{k_B T}\right) \approx 1.55 \times 10^{-4}\ s$$

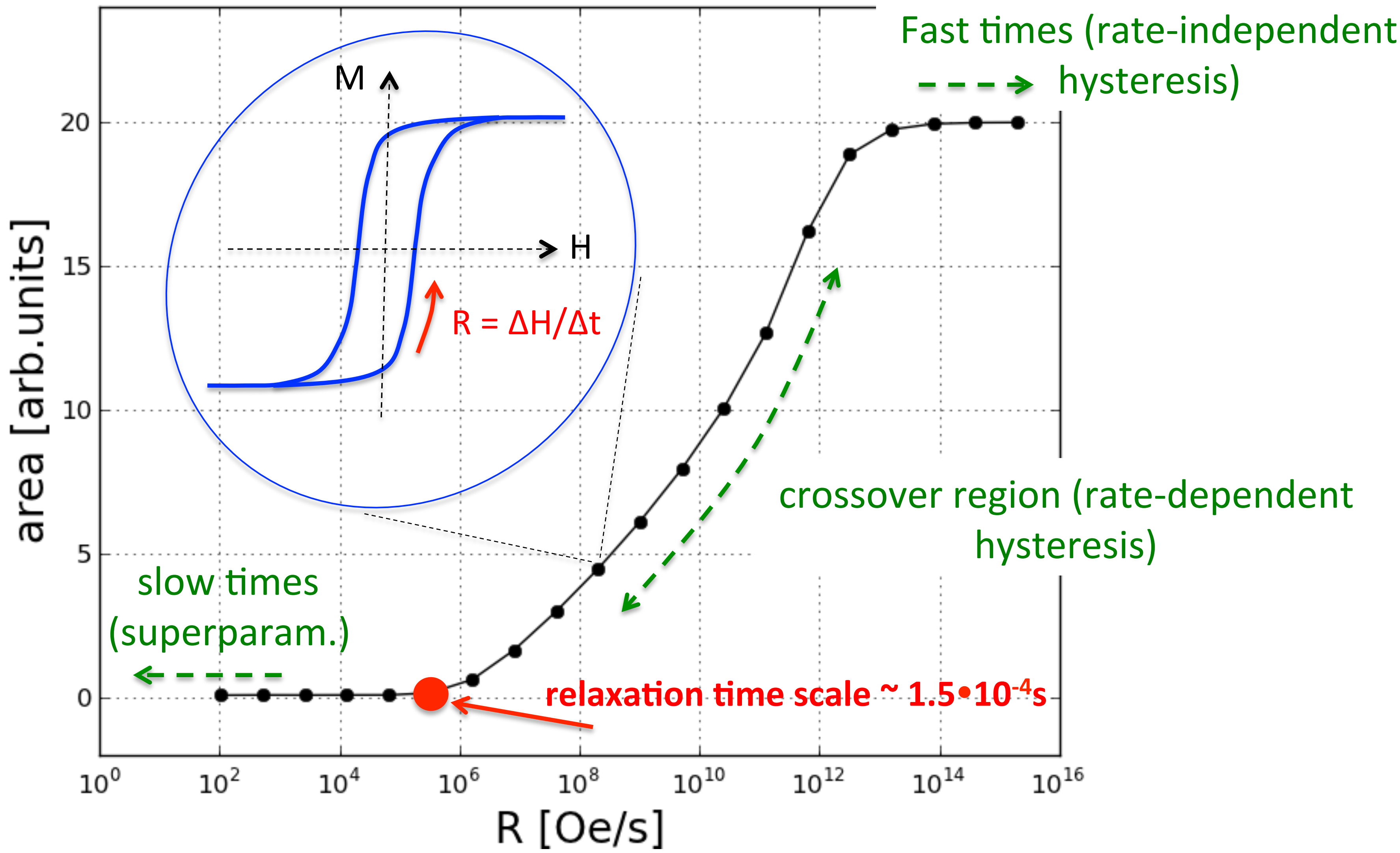
900 part; M_S = 400 emu/cc (Magnetite), K = 10^6 erg/cc, d = 10nm; T = 300 K; $f_0 = 10^{-9}\ s^{-1}$

Hysteresis loop: non-interacting case

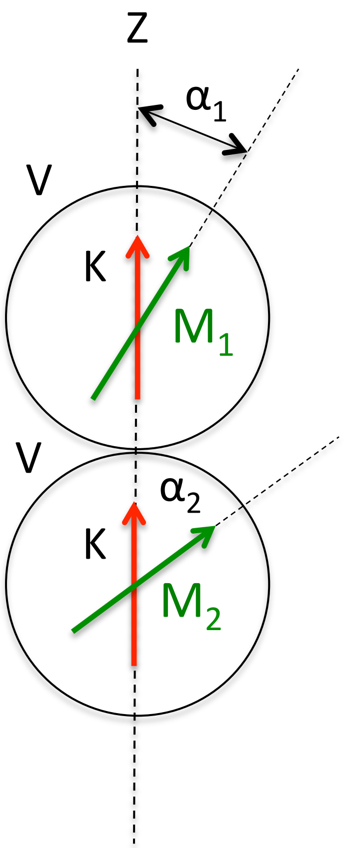
900 particles
M_S = 400 emu/cc (Magnetite)
K = 10^6 erg/cc, d = 10nm
T = 300 K, $f_0 = 10^{-9}\ s^{-1}$



Hysteresis loop area vs rate: non-interacting case



Example II: 2 particle chain at H = 0 - Interactions



$$e = \frac{E}{KV} = \sin^2\alpha_1 + \sin^2\alpha_2 + I\left(\cos(\alpha_1 - \alpha_2) - 3\cos\alpha_1\cos\alpha_2\right)$$

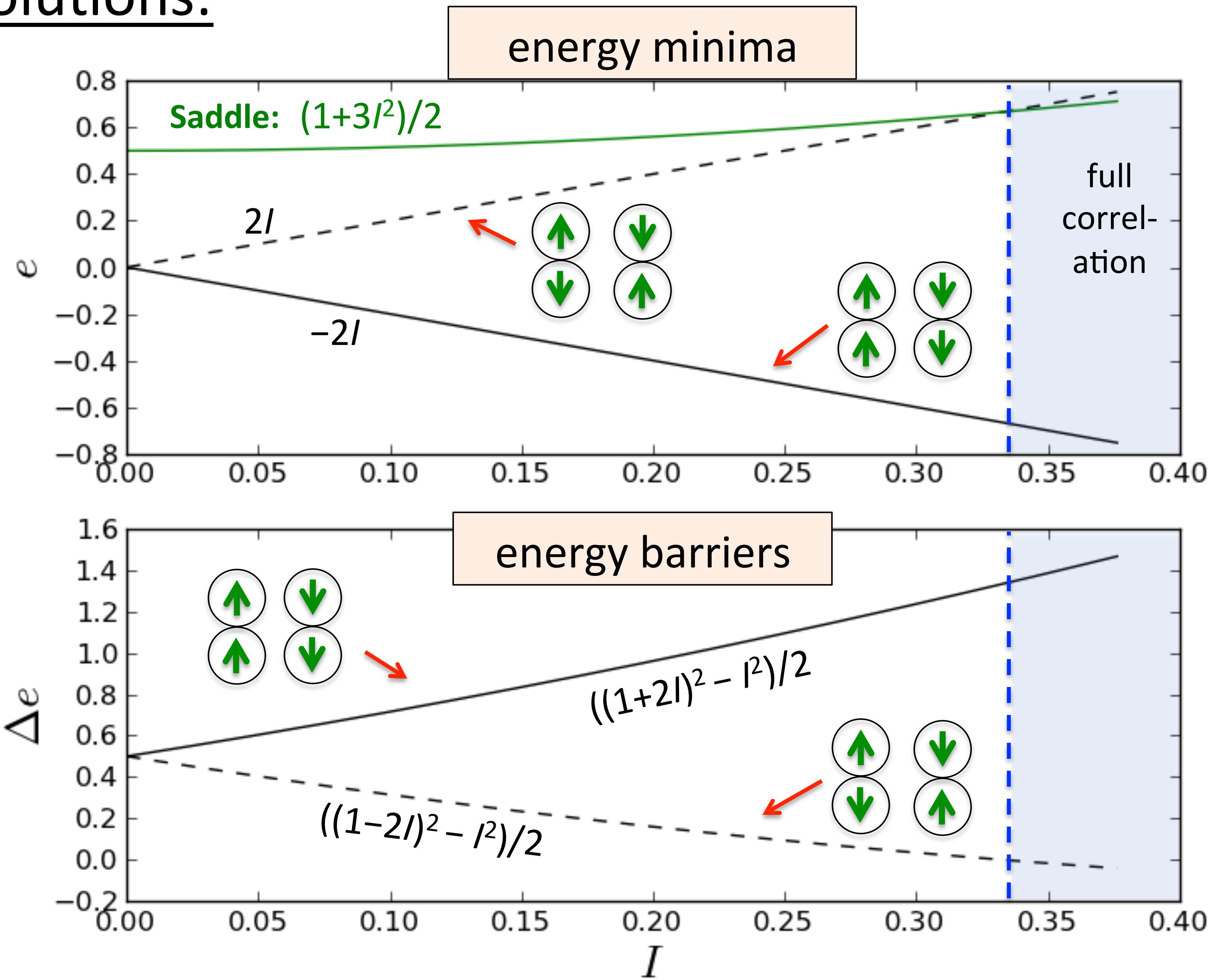
$$\frac{\partial e}{\partial \alpha_1} = 0 \qquad \frac{\partial e}{\partial \alpha_2} = 0$$

$$\sin(\alpha_1 + \alpha_2) = 0 \quad \& \quad \sin(\alpha_1 - \alpha_2) = 0$$

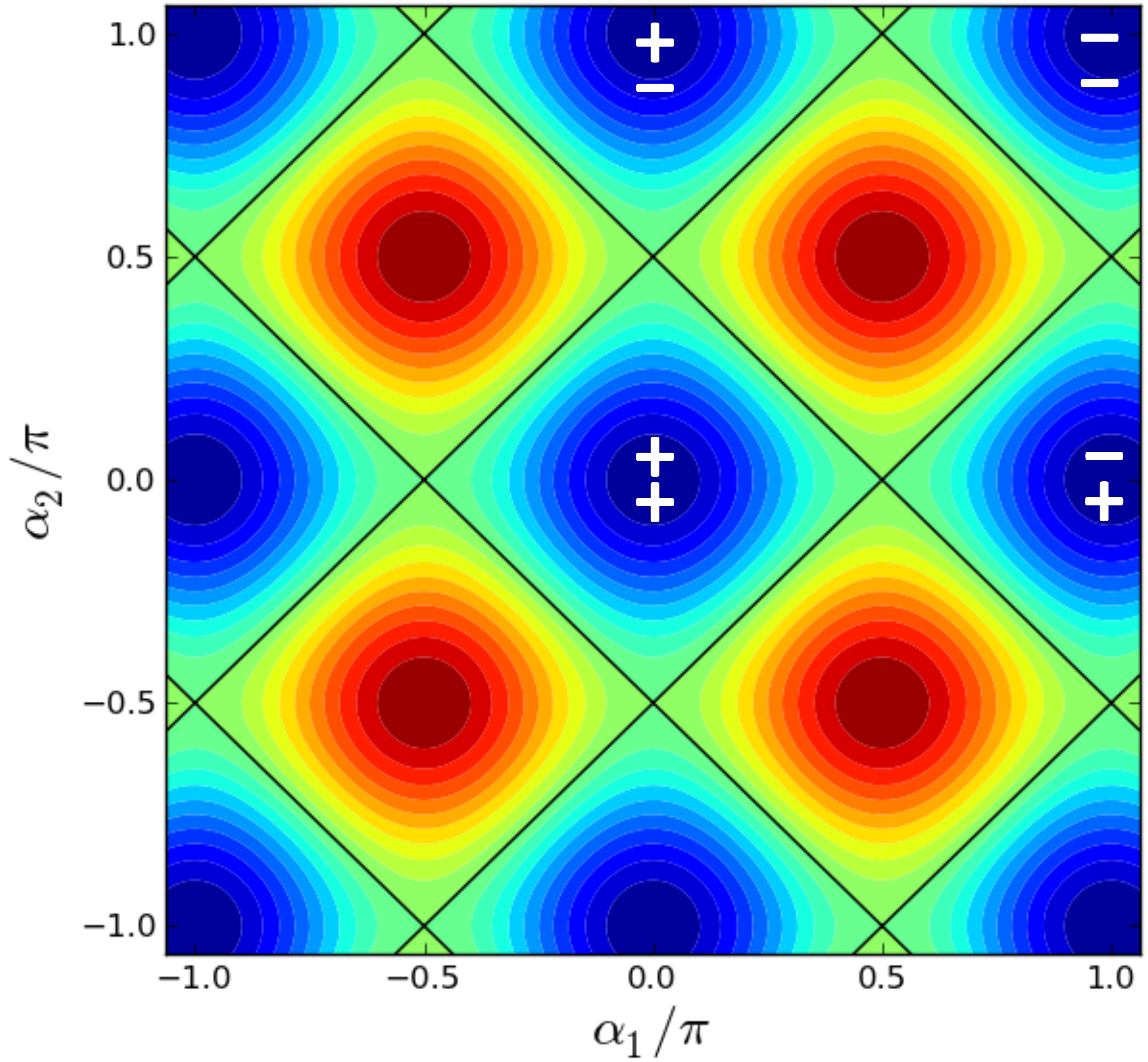
$$\cos(\alpha_1 + \alpha_2) = -\frac{1}{2}I \quad \& \quad \cos(\alpha_1 - \alpha_2) = -\frac{3}{2}I$$

$$I = \frac{M_S V}{4\pi a^3 H_K}$$

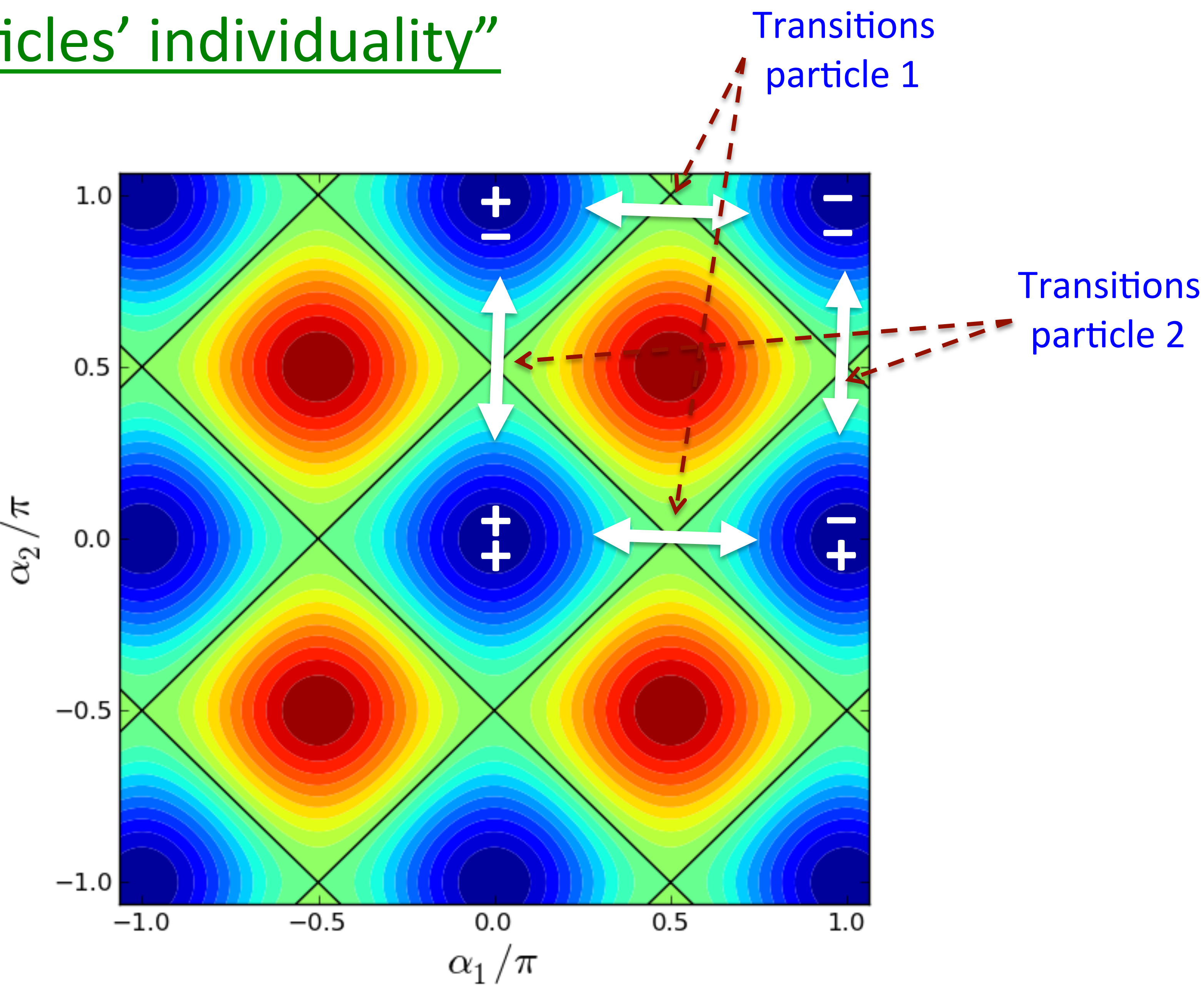
Solutions:

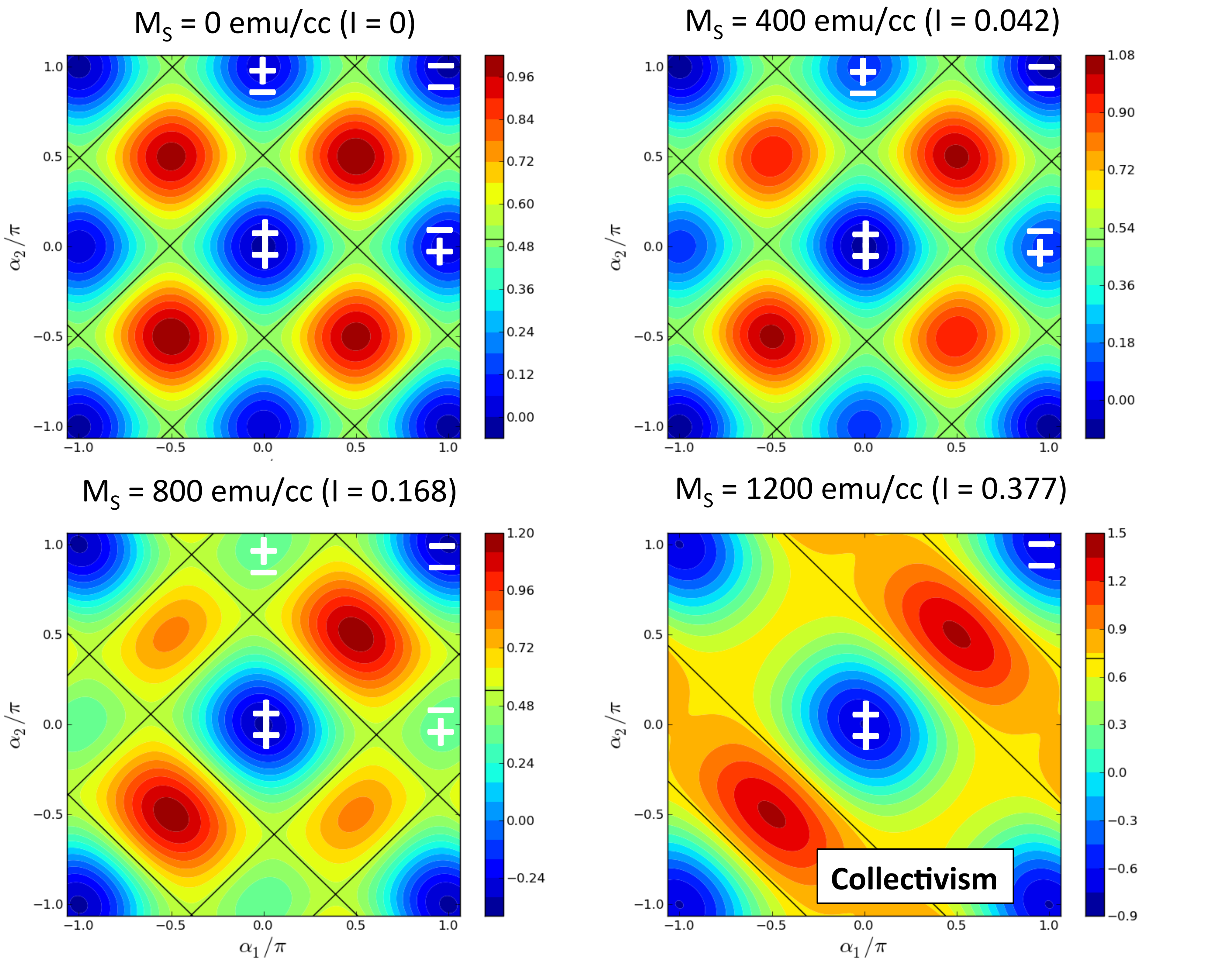

energy minima
Saddle: (1+3I²)/2
2I
−2I
full correl-ation
e
energy barriers
((1+2I)² − I²)/2
((1−2I)² − I²)/2
Δe
I
0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40

Look at the energy surface when I = 0:



Energy surface I = 0:
“particles’ individuality”





M_S = 0 emu/cc (I = 0)
M_S = 400 emu/cc (I = 0.042)
M_S = 800 emu/cc (I = 0.168)
M_S = 1200 emu/cc (I = 0.377)
α_1/π
α_2/π
Collectivism

Do we expect our algorithm to work in the interacting particle case? Yes if:

1. Well defined single particle transitions – *convergence to equilibrium (thermodynamic) state at long times (or for slow rates)*

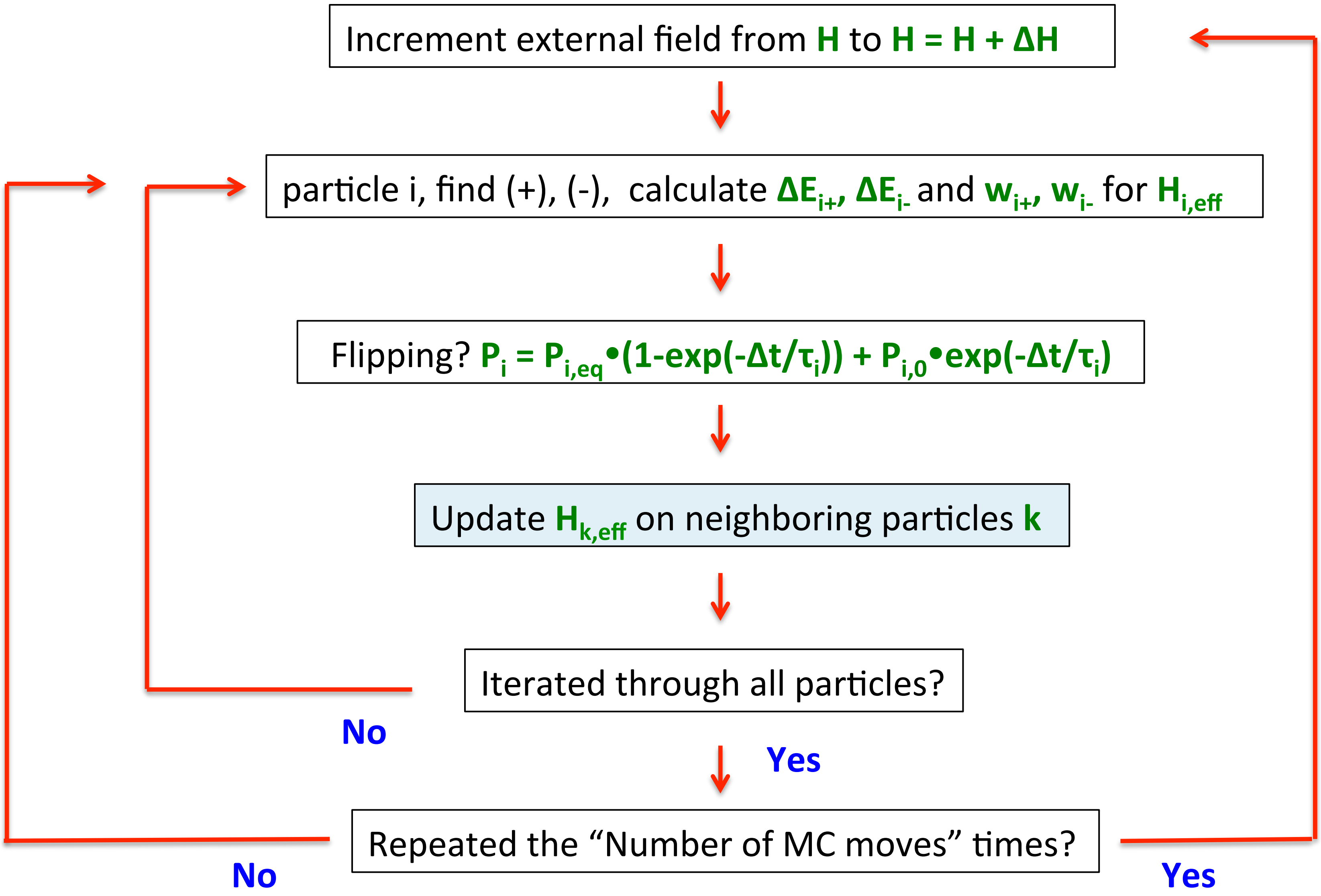
2. Energy barriers corresponding to individual transitions well described by a single particle Stoner-Wohlfarth theory – *accuracy of physical description*

1) & 2) satisfied if sufficiently weak interactions:

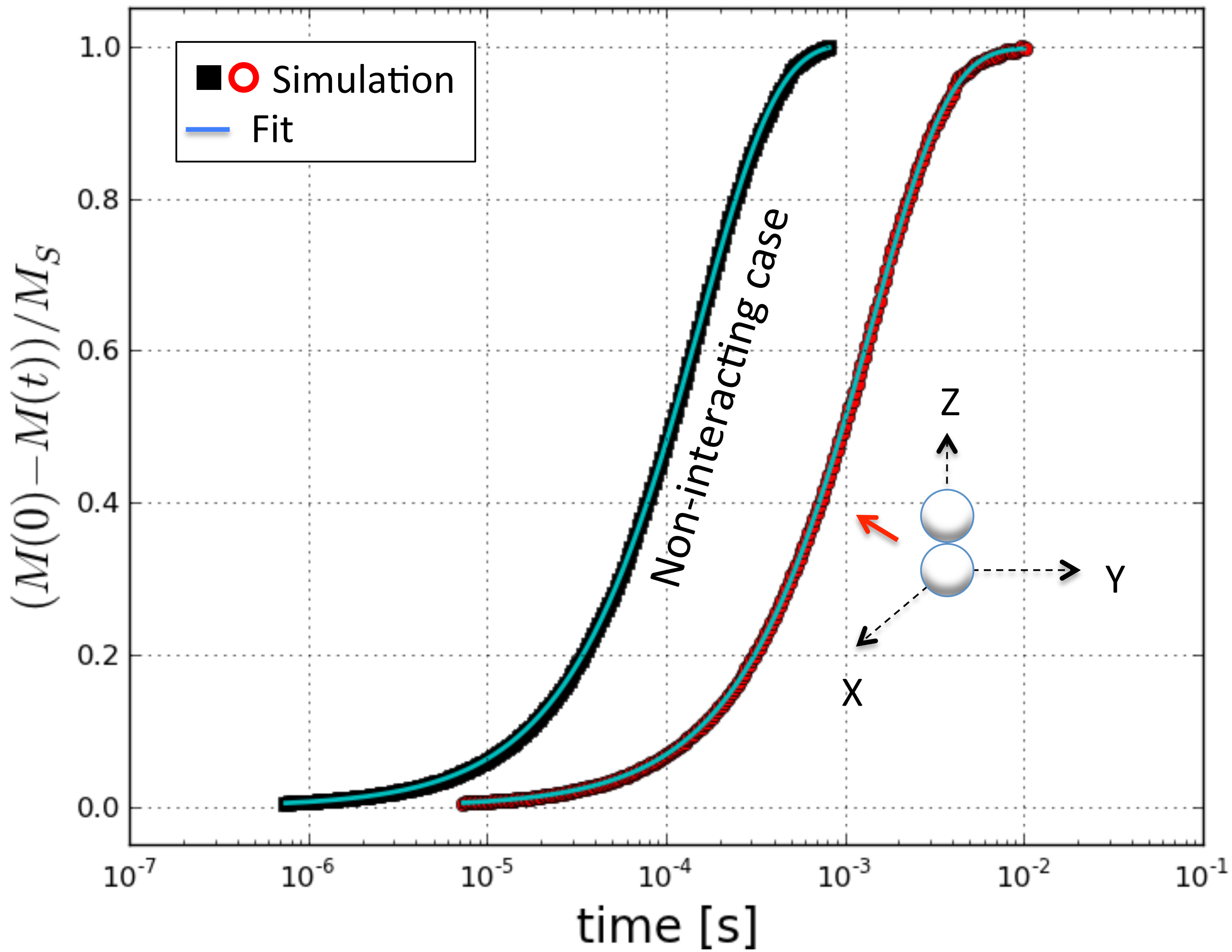
Rule of thumb:

$I < 0.1$

How we compute hysteresis loops: iterative solution of the master equation



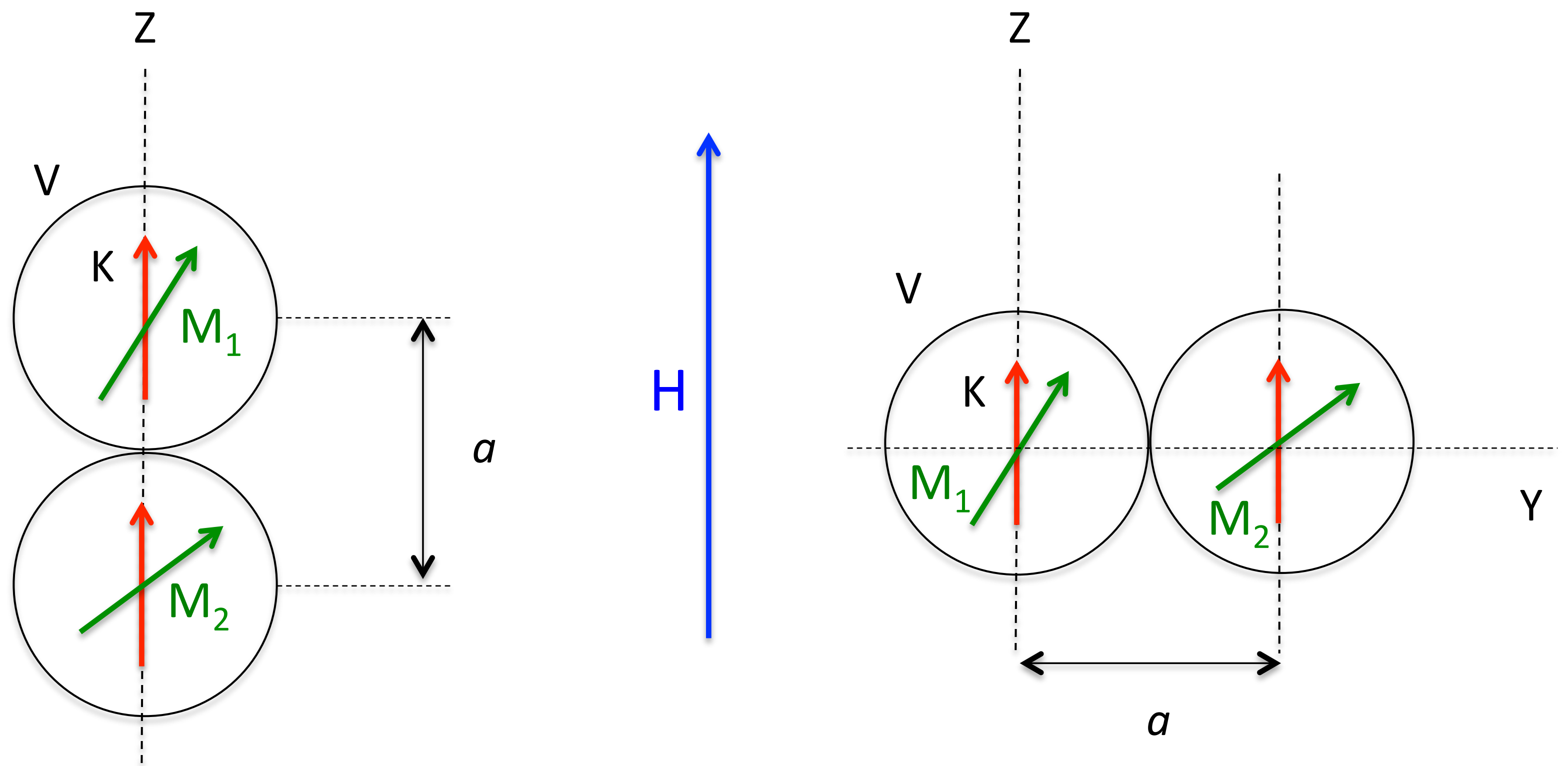
Relaxation:



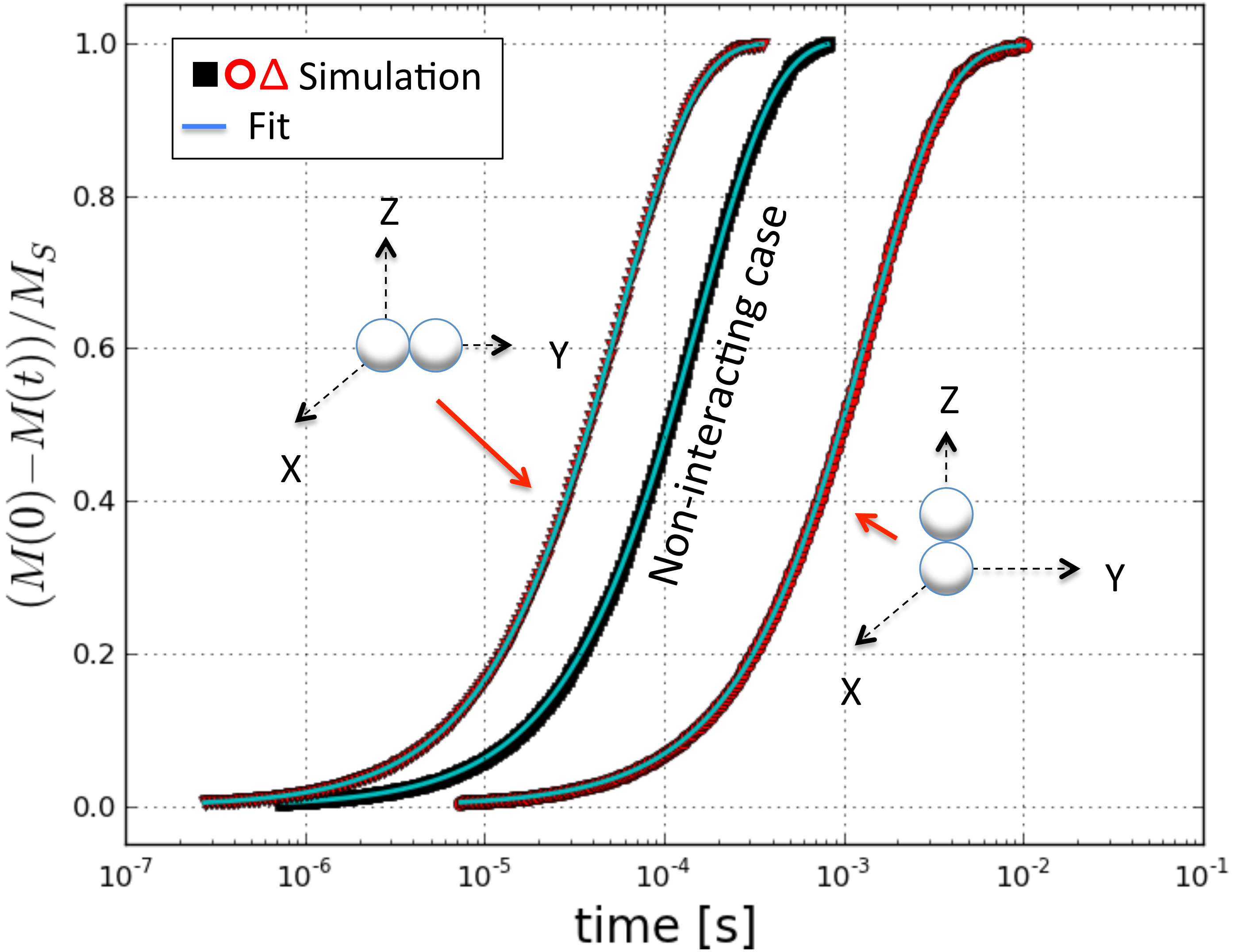
900 part; M_S = 400 emu/cc (Magnetite), K = 10^6 erg/cc, d = 10nm; T = 300 K; $f_0 = 10^{-9}$ s^{-1}

Directional dependence of dipolar interactions?

$$e_{dd} = I_{ij}\left[\hat{M}_i \cdot \hat{M}_j - 3\left(\hat{M}_i \cdot \hat{a}\right)\left(\hat{M}_j \cdot \hat{a}\right)\right] \qquad I_{ij} = \frac{V_j M_S}{4\pi a^3 H_{K,i}}$$



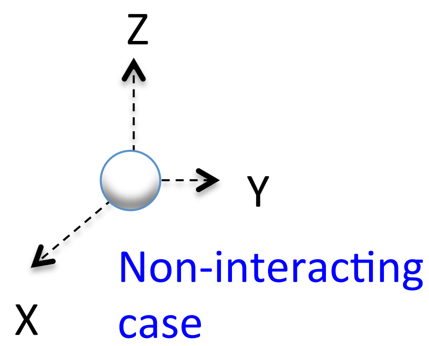
Relaxation:

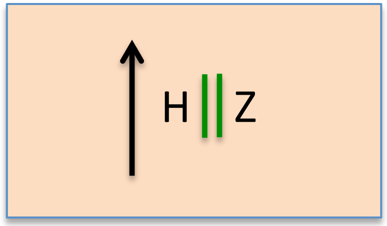


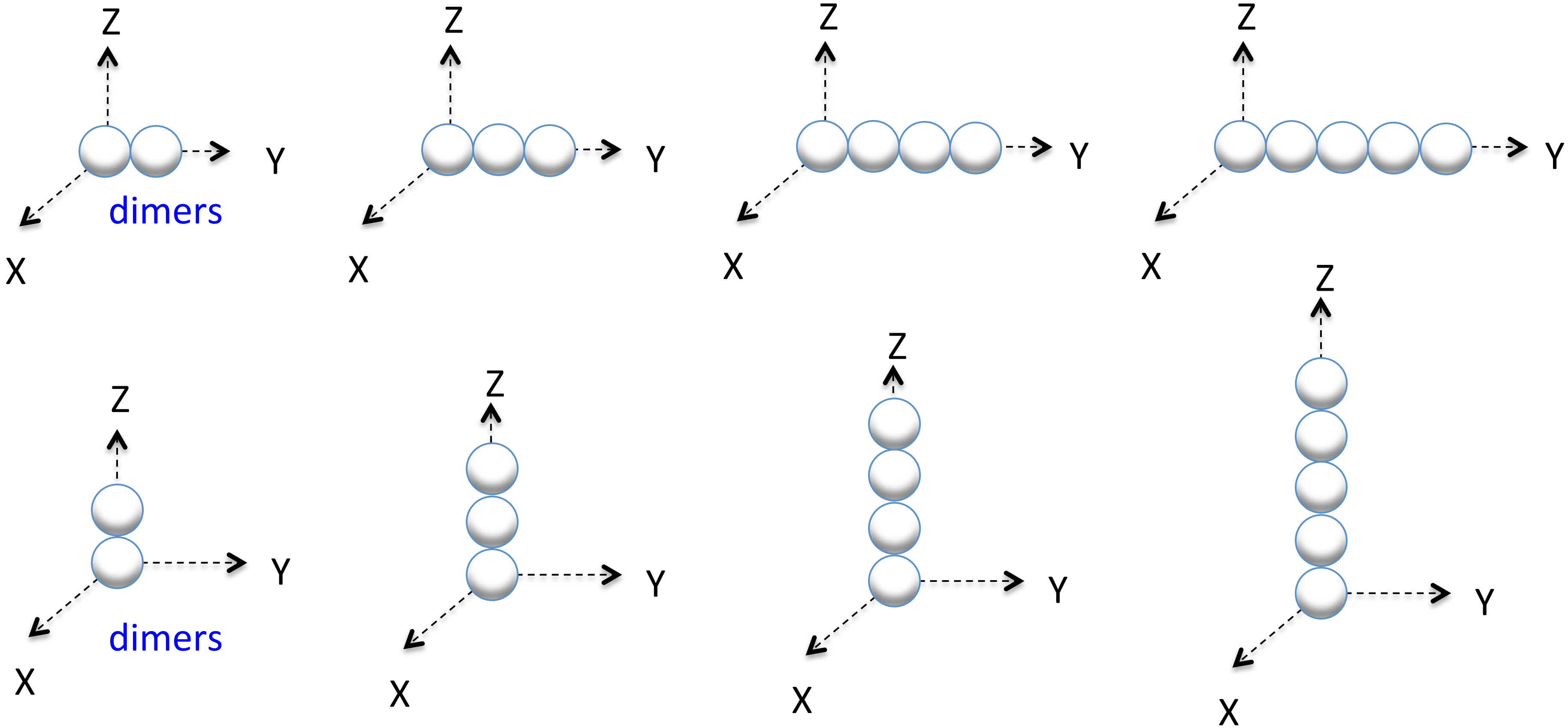
Simulation
Fit
1.0
0.8
0.6
0.4
0.2
0.0
$(M(0)-M(t))/M_S$
Z
Y
X
Non-interacting case
Z
Y
X
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
time [s]

What kind of mag. particle chains?

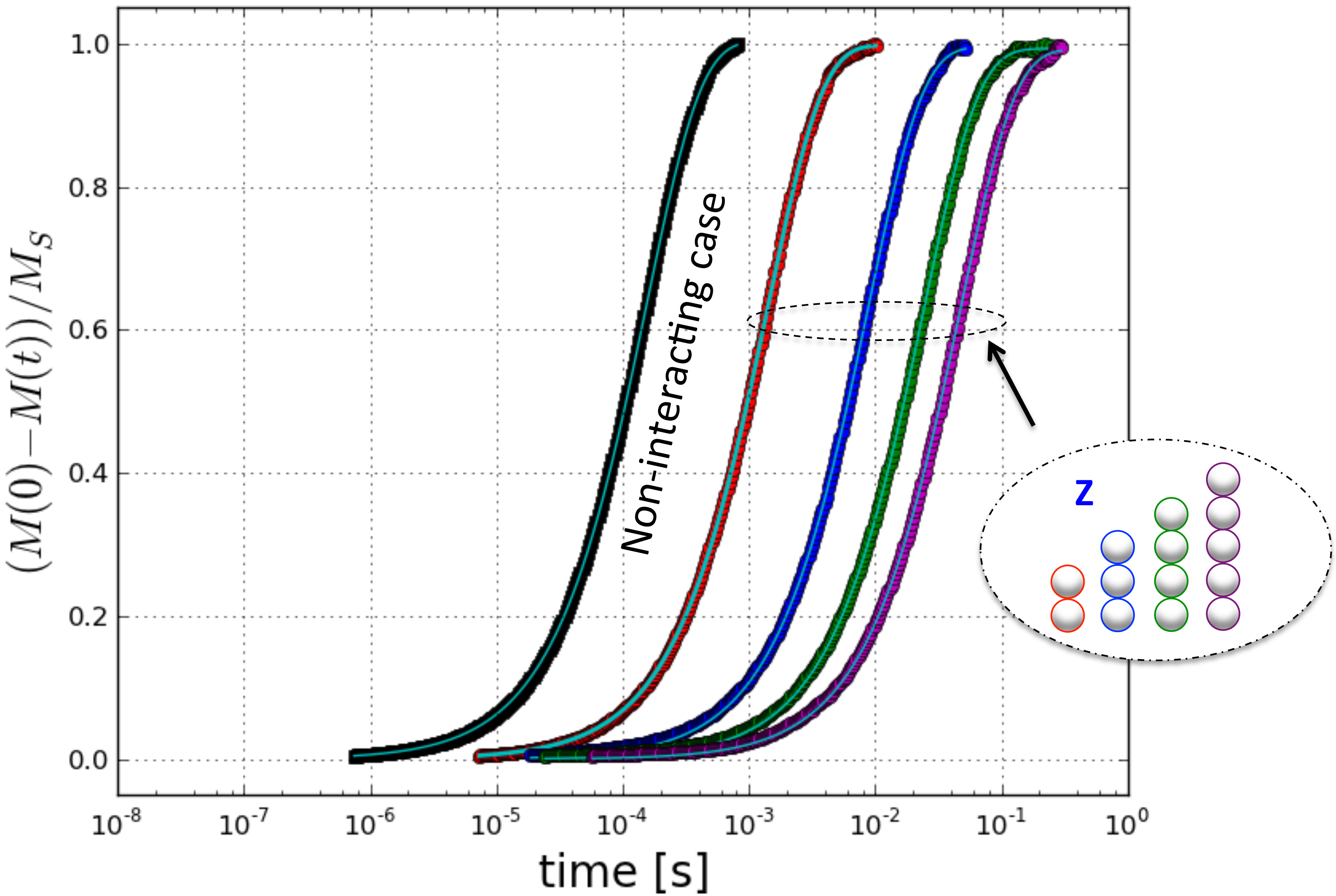
+ ensembles of chains
(interaction only within the chain)





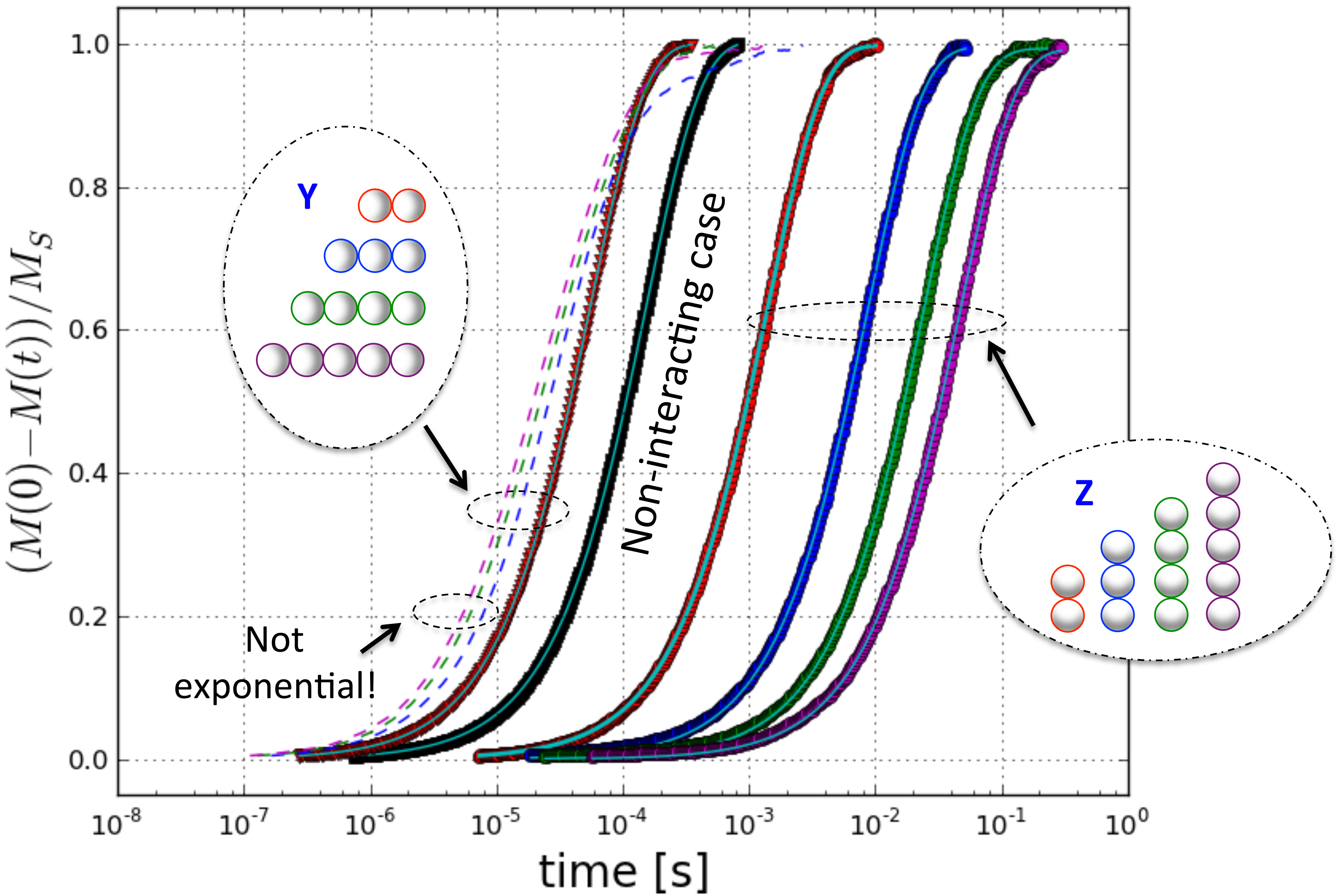


Relaxation:



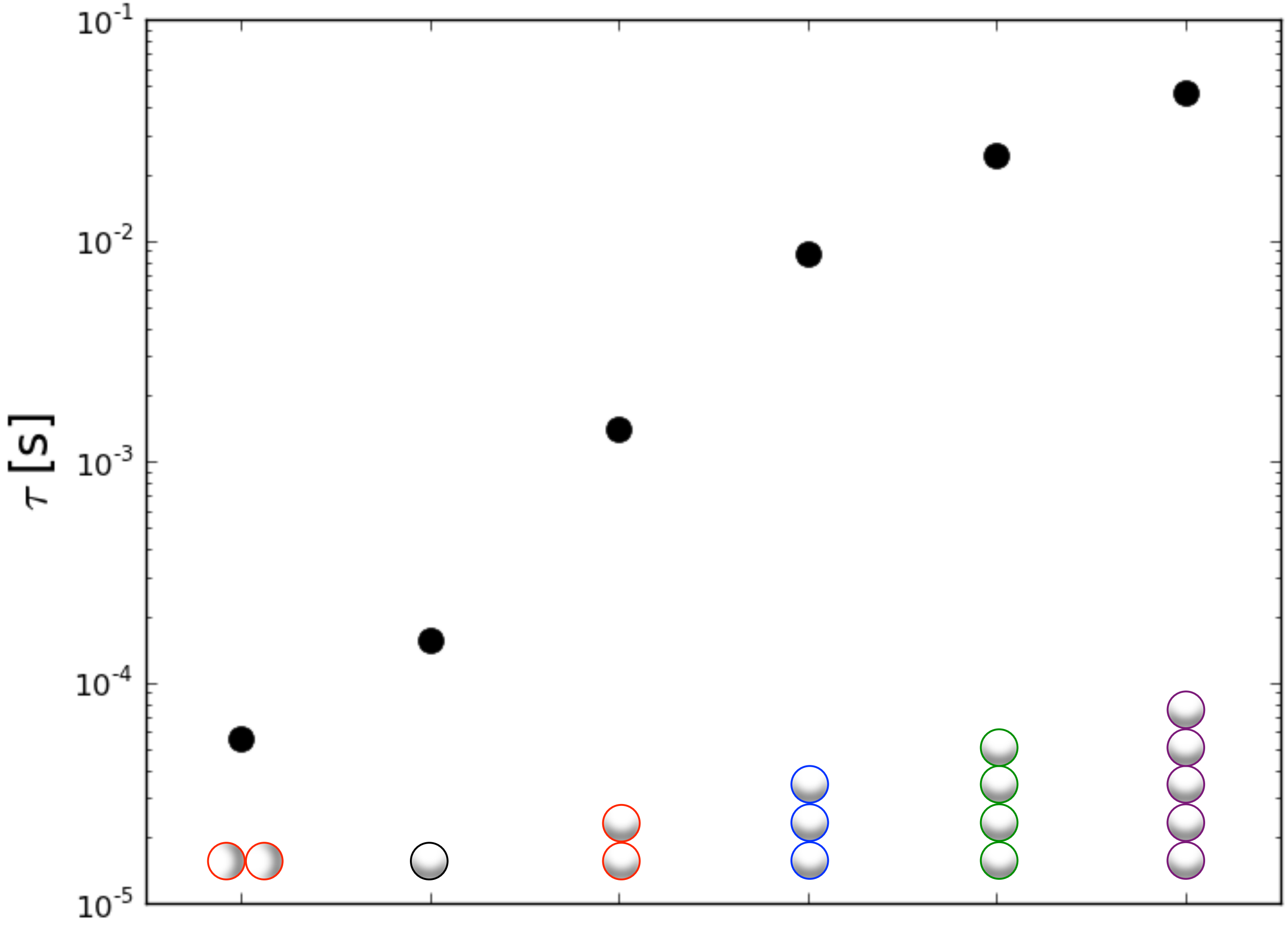
1.0
0.8
0.6
0.4
0.2
0.0
$(M(0)-M(t))/M_S$
Non-interacting case
Z
10^{-8} 10^{-7} 10^{-6} 10^{-5} 10^{-4} 10^{-3} 10^{-2} 10^{-1} 10^{0}
time [s]

Relaxation:

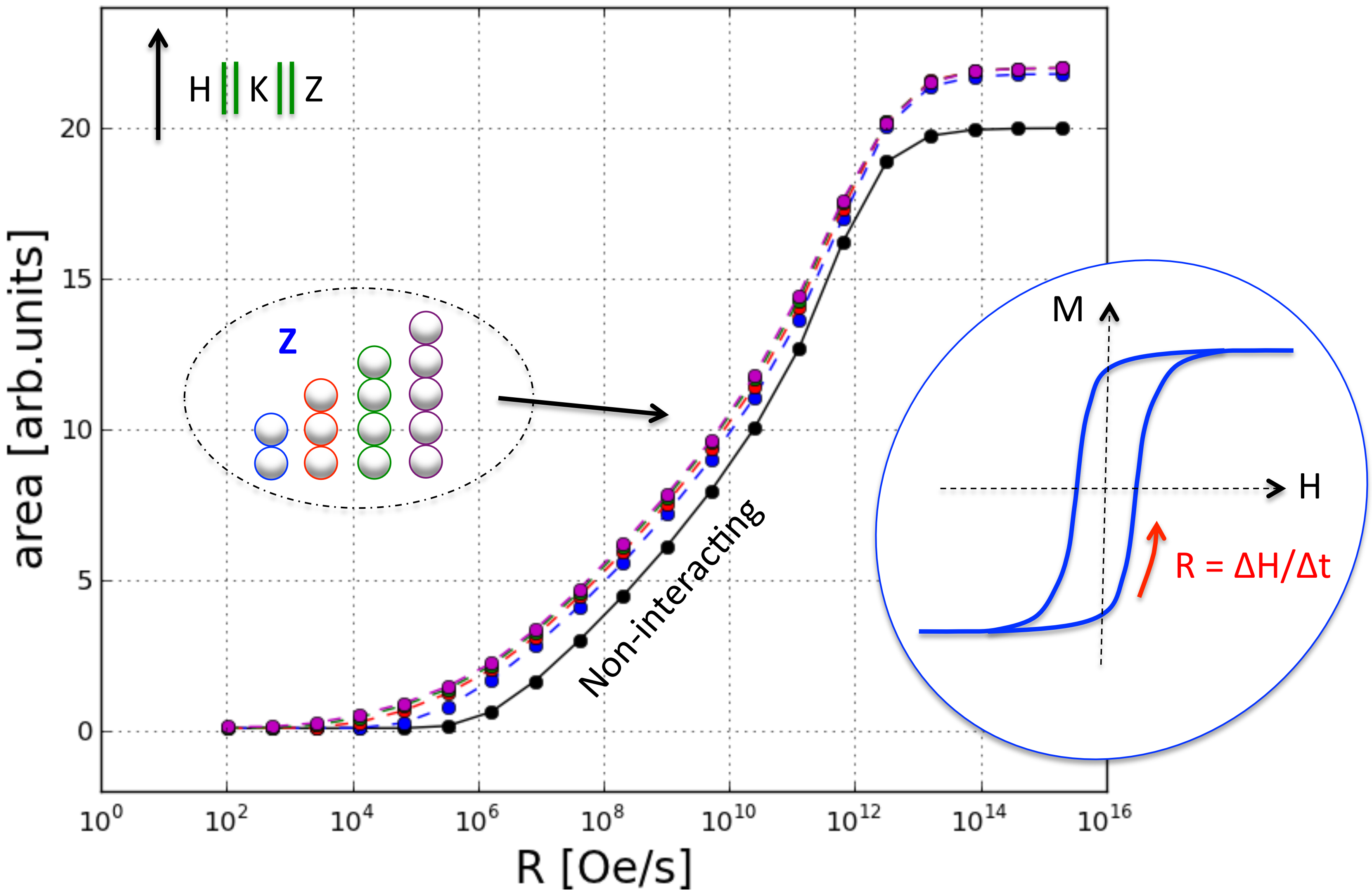


1.0
0.8
0.6
0.4
0.2
0.0
$(M(0)-M(t))/M_S$
Y
Z
Non-interacting case
Not
exponential!
10^{-8}
10^{-7}
10^{-6}
10^{-5}
10^{-4}
10^{-3}
10^{-2}
10^{-1}
10^{0}
time [s]

Relaxation time from the exponential fit:

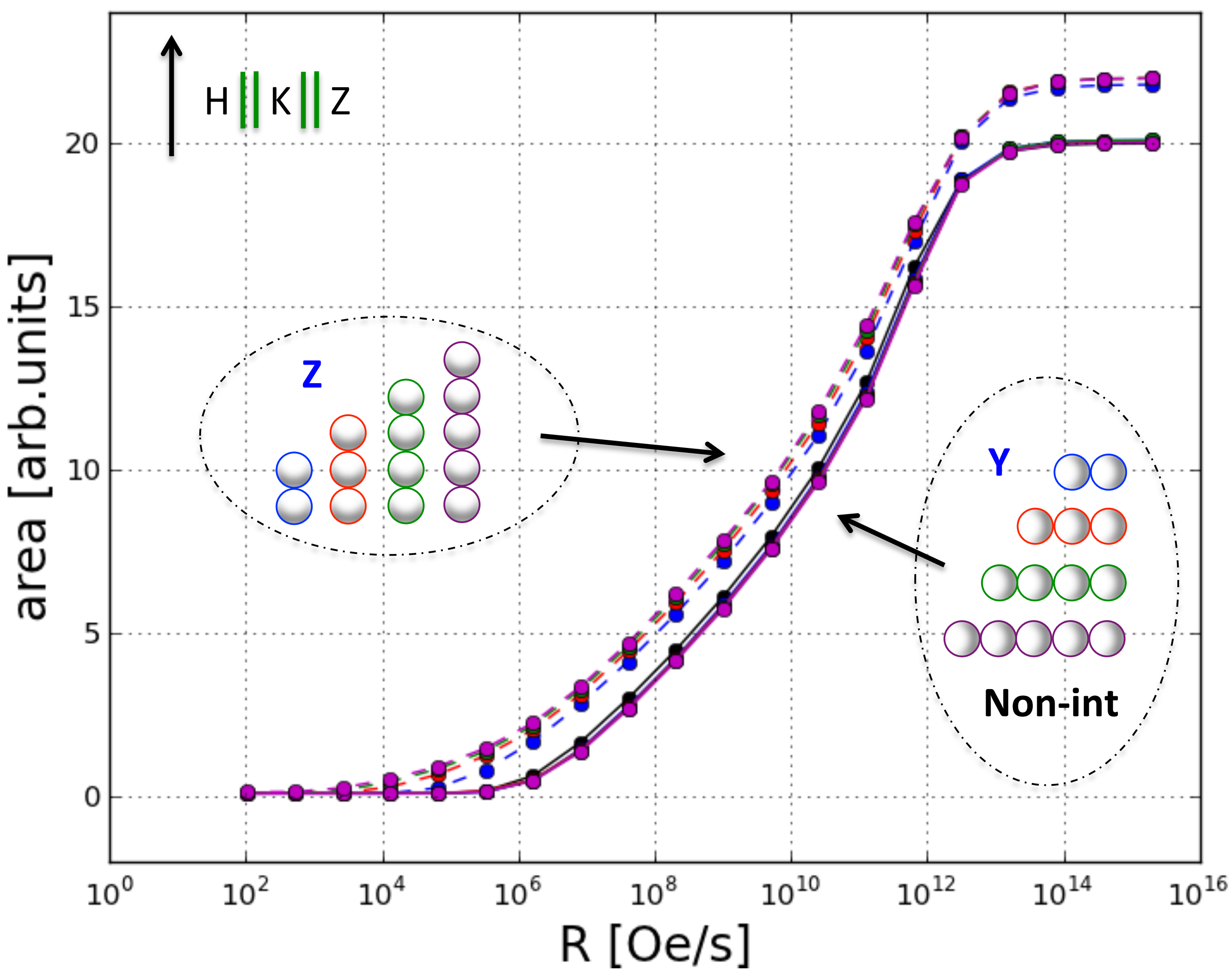


Hysteresis loop area vs rate: Z-oriented chains



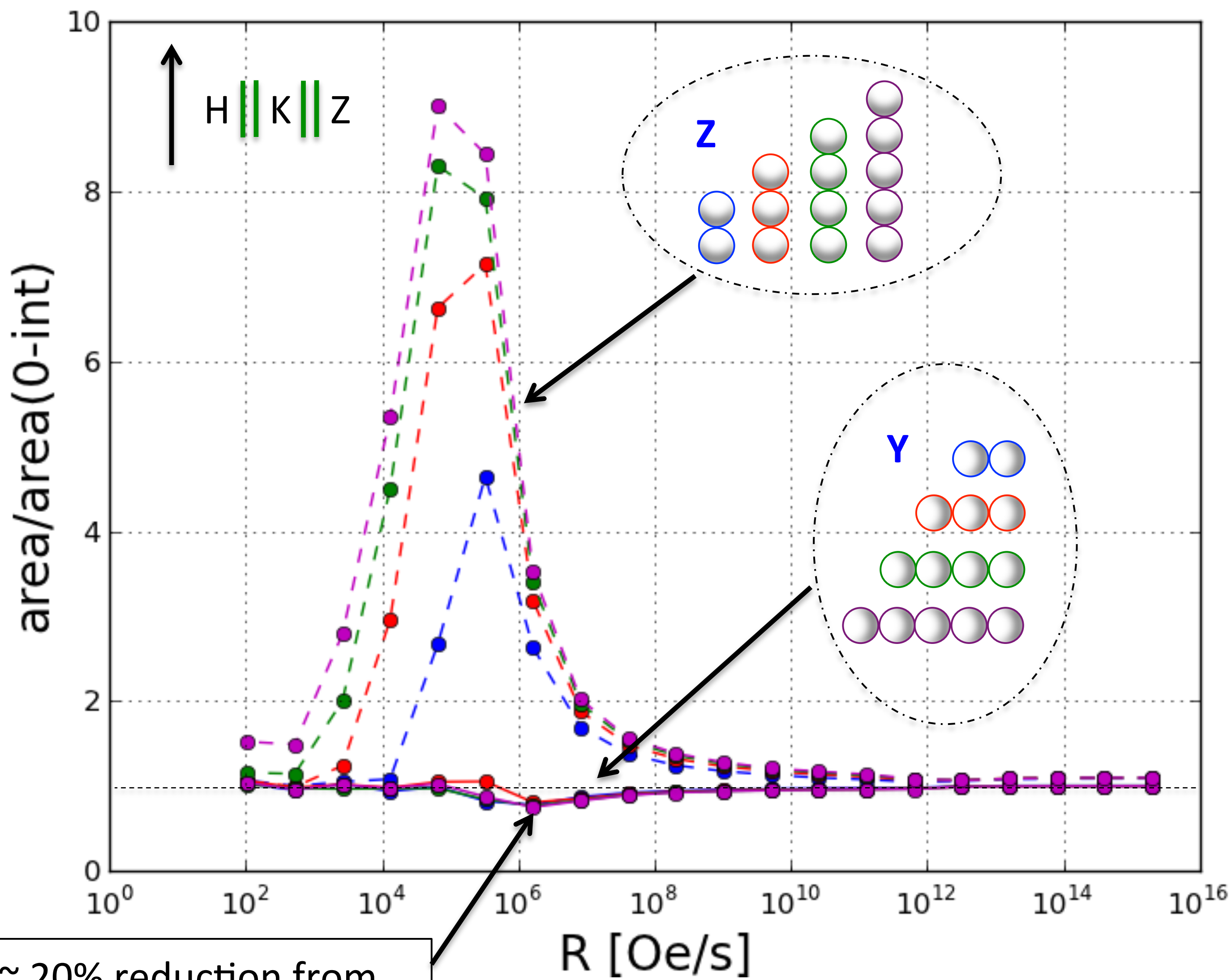
900 part; M_S = 400 emu/cc (Magnetite), K = 10^6 erg/cc, d = 10nm; T = 300 K; $f_0 = 10^{-9}$ s^{-1}

Hysteresis loop area vs rate: Z&Y-oriented chains



900 part; M_S = 400 emu/cc (Magnetite), K = 10^6 erg/cc, d = 10nm; T = 300 K; $f_0 = 10^{-9}$ s^{-1}

Comparison with respect to the non-interacting case:



~ 20% reduction from the non-int case

Conclusions:

- Kinetic Monte-Carlo technique which allows computational investigation of the rate-dependent hysteresis behavior of magnetic nanoparticle structures

- Dipolar interactions determine relaxation time scales and hysteresis losses => dependence on
  - the orientations of chains with respect to the external field
  - a particle number within a chain
  - a particle arrangement – chains/clusters
  - anisotropy axis orientation

- Optimization of hysteresis by particle chain/cluster selection (HGMS, …)

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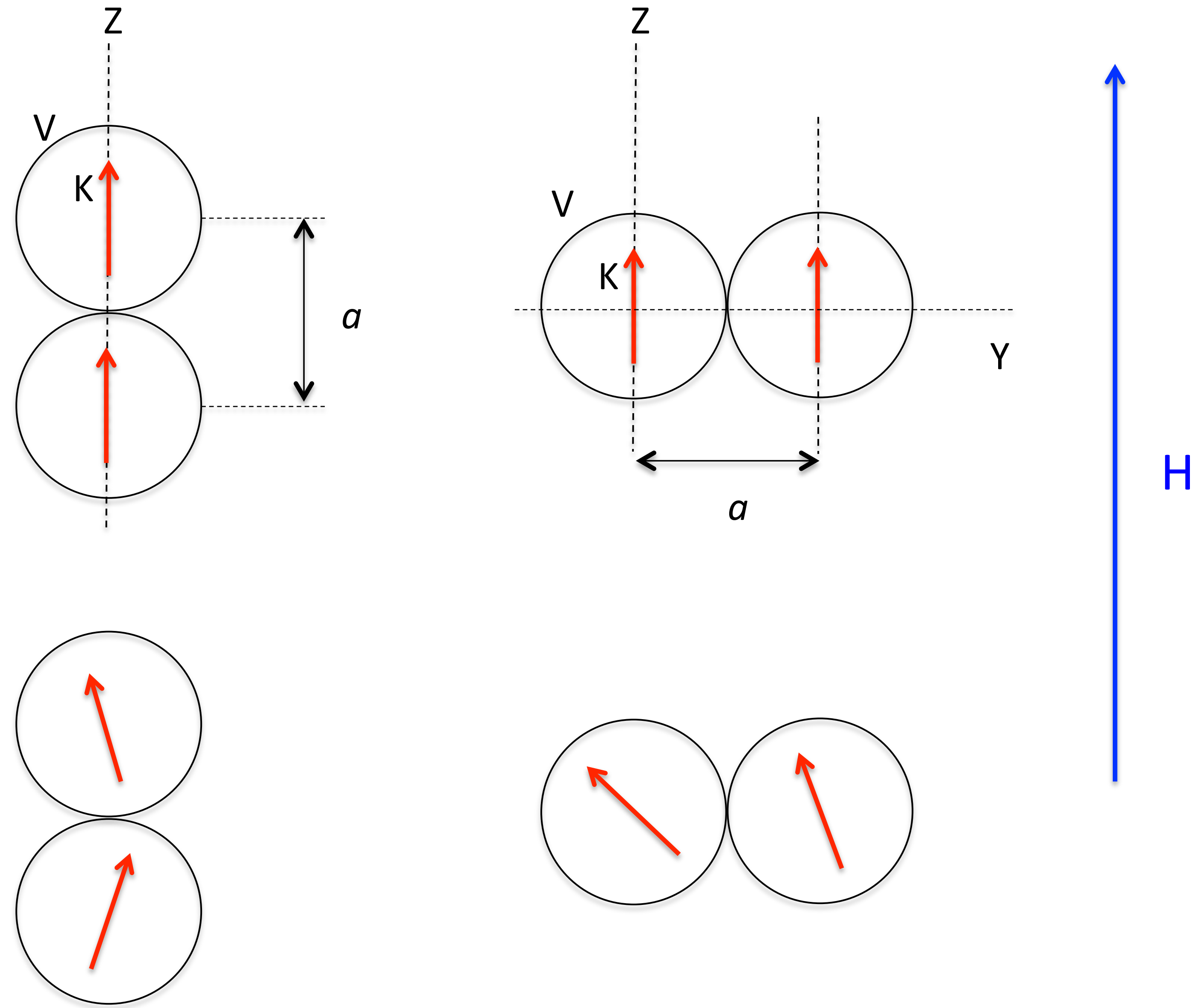
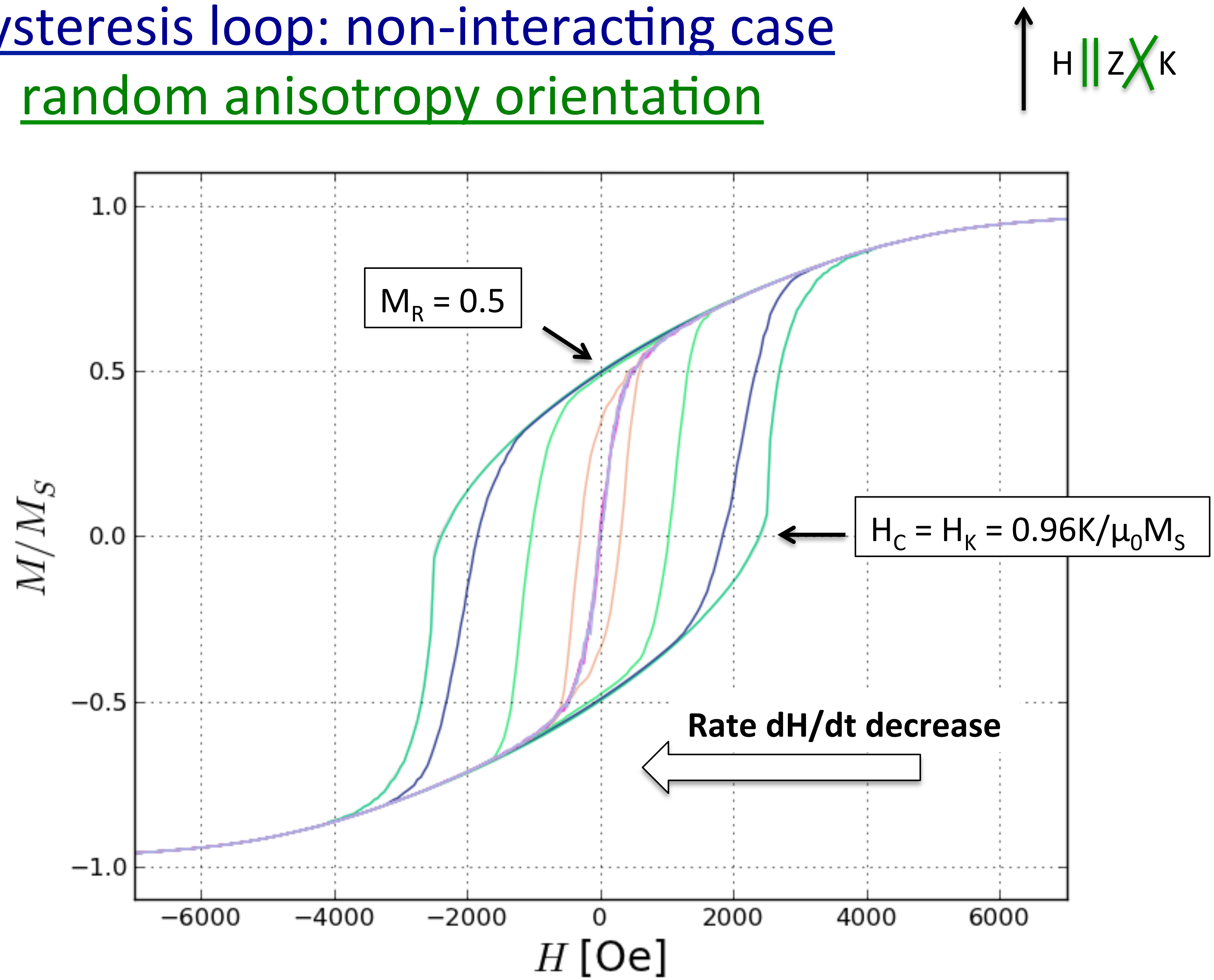
Random anisotropy axis orientation

So far only:

How about:

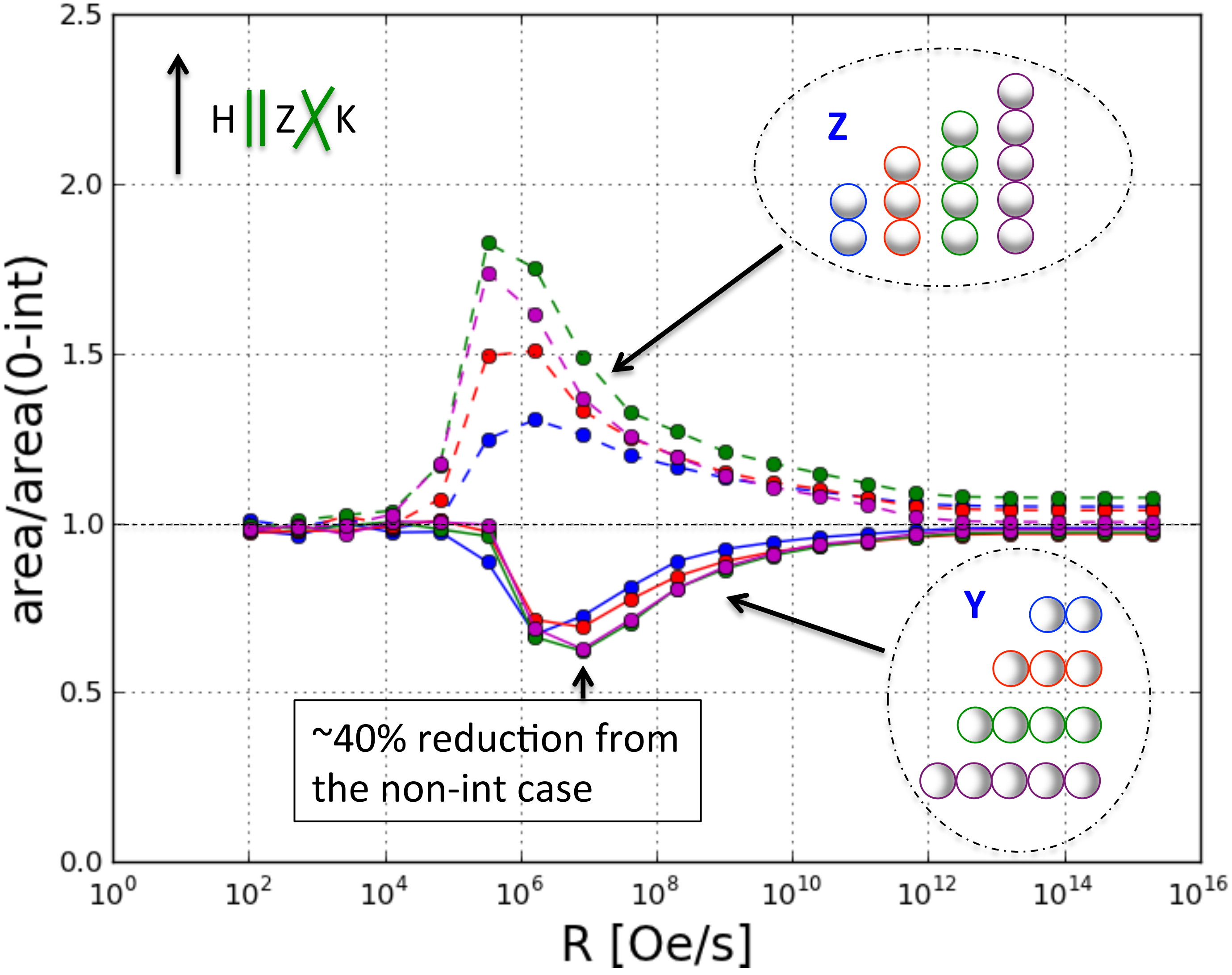


Hysteresis loop: non-interacting case
random anisotropy orientation

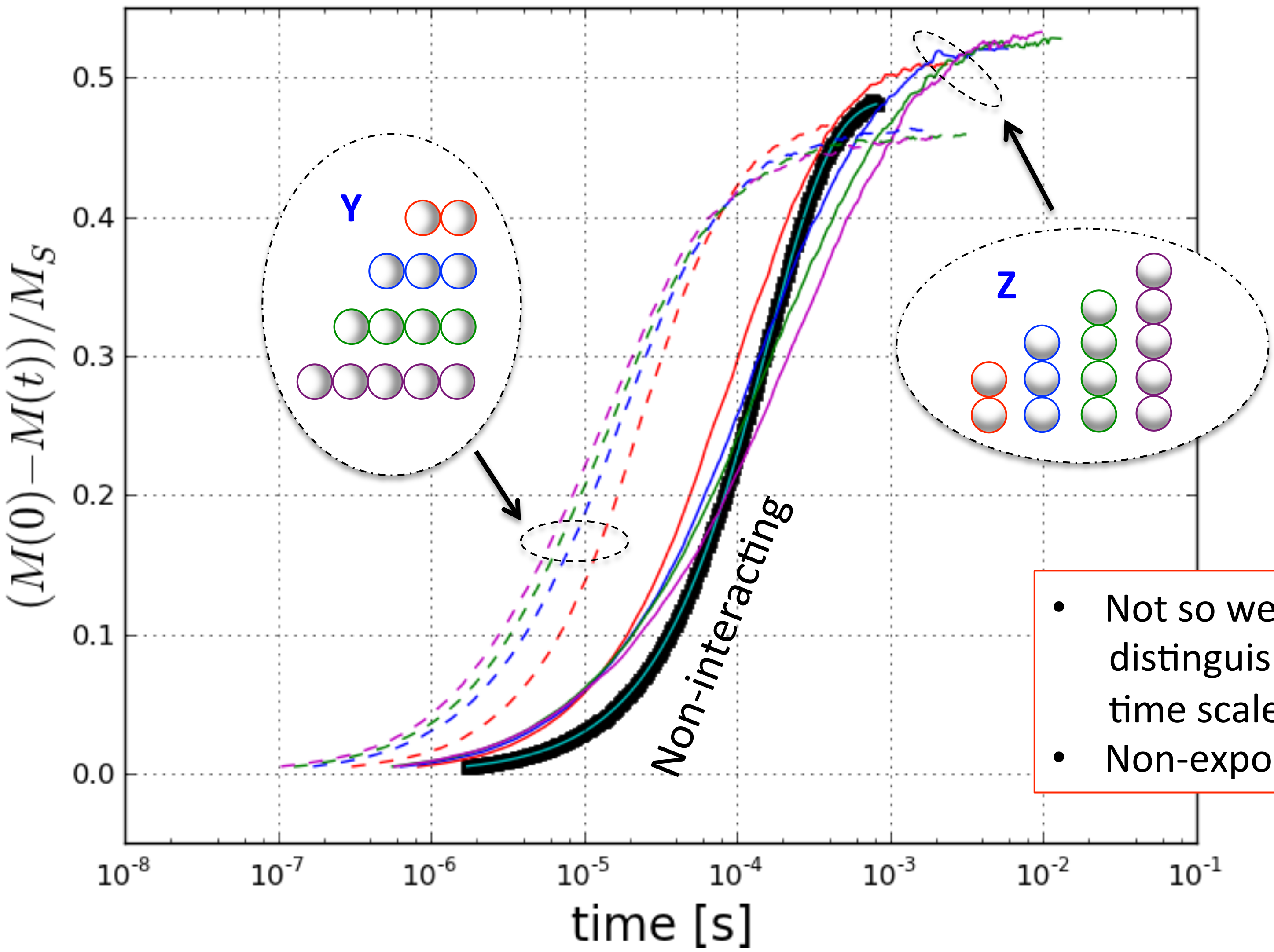


900 part; M_S = 400 emu/cc (Magnetite), K = 10^6 erg/cc, d = 10nm; T = 300 K; $f_0 = 10^{-9}$ s^{-1}

Comparison with respect to the non-interacting case: random anisotropy orientation



Relaxation characteristics:



- Not so well distinguishable time scales
- Non-exponential