Metastability and finite-size effects in magnetization switching

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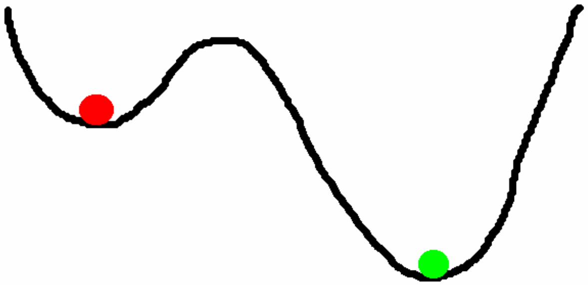
http://www.physics.fsu.edu/users/rikvold/info/rikvold.htm

What is a metastable phase?



1. The free energy is **not** fully minimized
2. Only **one** thermodynamic phase is present
3. Equilibrium thermodynamics holds for **weak and slow** disturbances
4. The average lifetime is **very long**
5. Escape is **irreversible**: return to the metastable phase is extremely improbable

The first observation:

D.G. Fahrenheit, Proc. Roy. Soc. London **33**, 78 (1724)

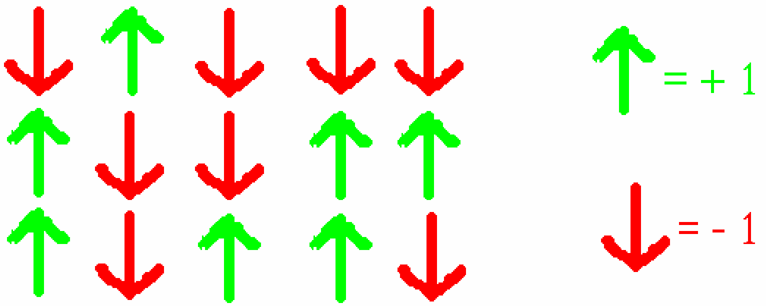
VIII. *Experimenta & Obſervationes de Congelatione aquæ in vacuo factæ a* D. G. Fahrenheit, R. S. S.

INter plurima admiranda Naturæ Phœnomena aquarum congelationem non minoris momenti eſſe ſemper judicavi; hinc ſæpe experiundi cupidus fui, quinam effectus frigoris futuri eſſent, ſi aqua in ſpatio ab aere vacuo clauderetur. Et quoniam dies ſecundus, tertius & quartus *Martii*, (Styli V.) Anni 1721. ejuſmodi experimentis favebat, hinc ſequentes obſervationes & experimenta a me ſunt factæ.

Toy Models: Kinetic Ising Systems

Defined by simple Hamiltonian:

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} s_i s_j - H \sum_i s_i$$

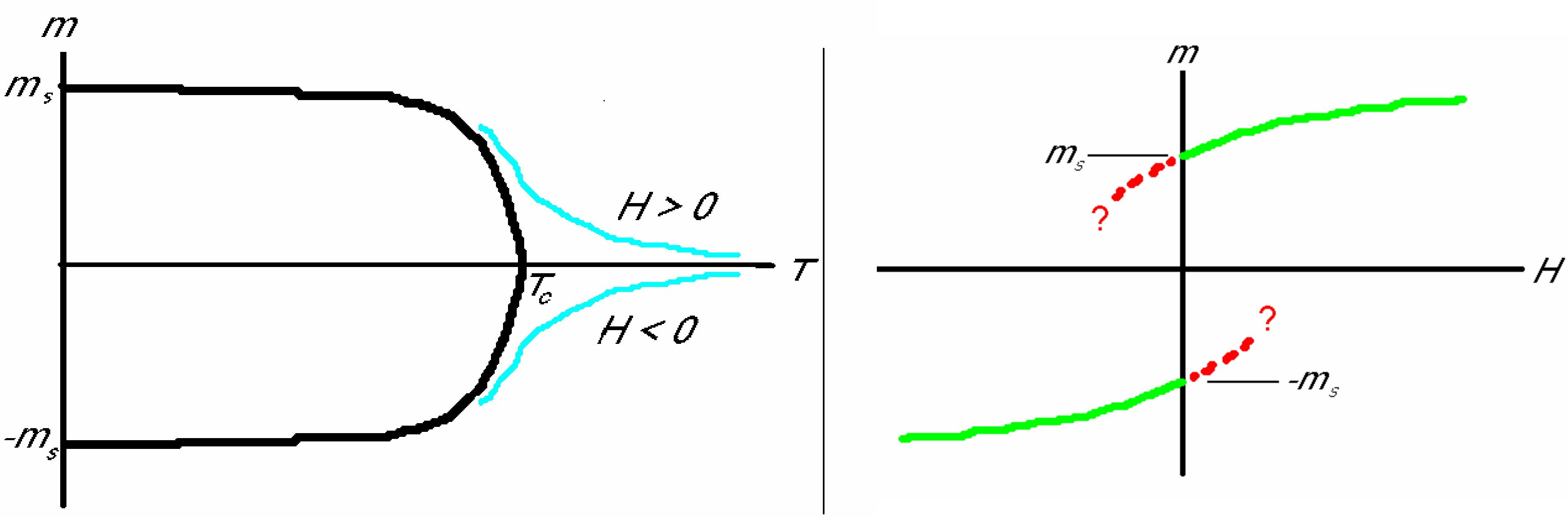


Order parameter is "magnetization:"

$$m = N^{-1} \sum_{i=1}^{N} s_i$$

Ising models have *phase transition*:

Below *critical temperature* T_c , *m* takes nonzero spontaneous value, $+/- m_s(T)$, for $H=0$



Below T_c: First-order phase transition with coexistence at $H=0$

Stochastic dynamics

Ising models have no intrinsic kinetics.
Construct one to mimic coupling to environment:

(Monte Carlo Simulation)

Randomly choose site i and **propose a flip**

Answer *YES* with probablity $W(s_i \rightarrow -s_i)$

Answer *NO* with probablity $1 - W(s_i \rightarrow -s_i)$

Two different W that lead to equilibrium:

Metropolis: $W(s_i \rightarrow -s_i) = \min[1, \exp(-\beta \Delta E_i)]$

Glauber or Heat Bath: $W(s_i \rightarrow -s_i) = \frac{\exp(-\beta \Delta E_i)}{1+\exp(-\beta \Delta E_i)}$
Where $\beta = 1/(k_\mathrm{B} T)$

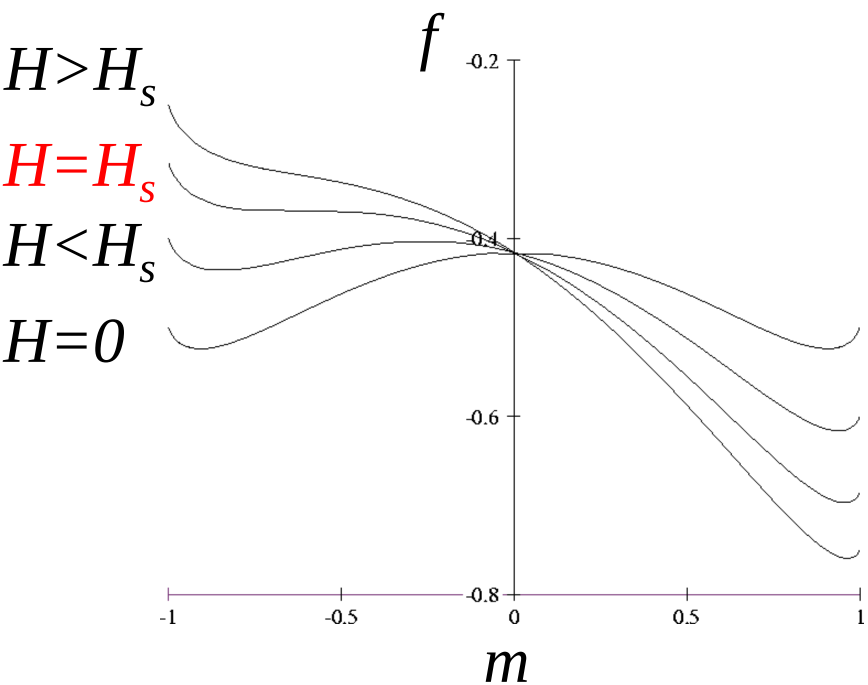
Mean-Field Picture

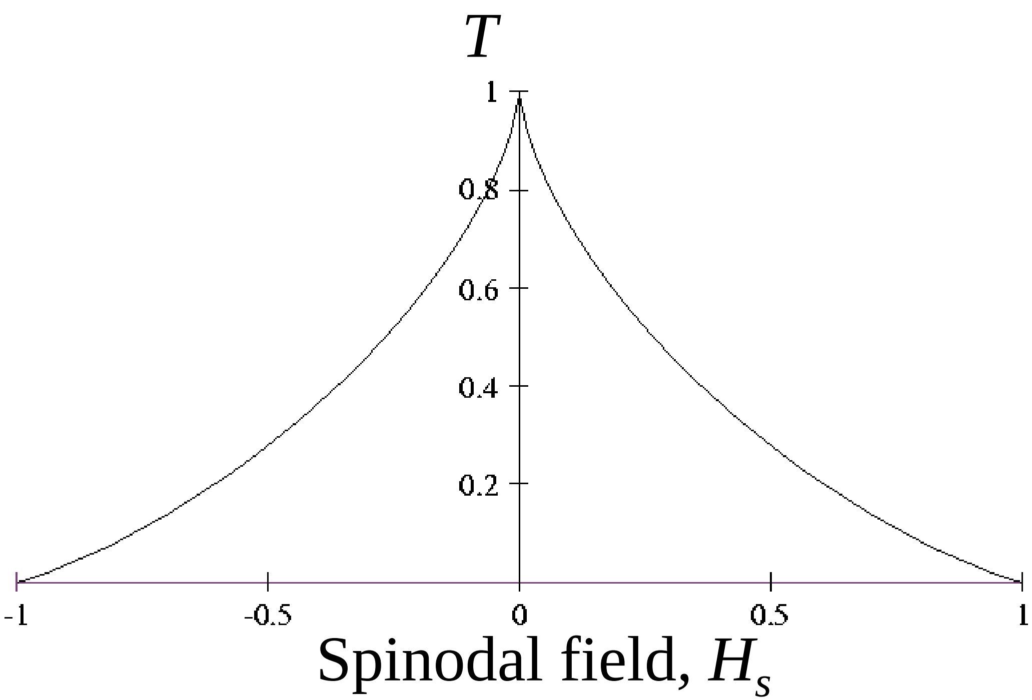
The system is completely *uniform*

The free-energy density depends only on *m* and *H*:

$$f = U(m) - Hm$$

A sharp spinodal field, H_s exists





Nucleation Theory

Most real systems are *not* uniform!

The metastable phase is unstable to fluctuations of *critical size*:

smaller fluctuations mostly decay;

larger fluctuations mostly grow.

Nucleation rate for critical fluctuations:

$$\Gamma = \mathcal{P} e^{-\beta F_c}$$

F_c : *Total* free energy of critical fluctuation.

$\mathcal{P}$: Pre-exponential factor.

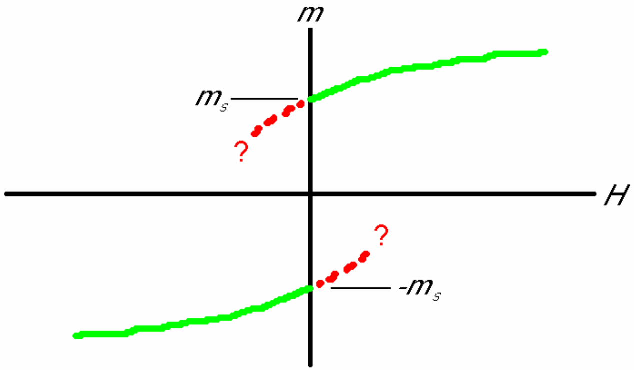
Some contributors to nucleation theory

- J.D. van der Waals (1873)
- J.C. Maxwell (1875)
- J.W. Gibbs (1876, 1878)
- M. Volmer and A. Weber (1926)
- R. Becker and W. Doering (1935)
- J.B. Zeldovich (1943)
- I. Frenkel (1939)
- J.S. Langer (1967, 1968, 1969)

Analytic Continuation **(Langer)**

General result:

$$\Gamma = \frac{\beta\kappa}{\pi}|\mathrm{Im}\tilde{f}|$$



$\tilde{f}$: Analytic continuation of equilibrium free-energy density into metastable phase.

κ : Kinetic prefactor, depends on dynamics.

Mean-Field system near H_s

"Critical fluctuation" is *entire system*: $F_\mathrm{c} = Volume \times f$

$\Rightarrow$ The metastable lifetime is *infinite* for $H < H_\mathrm{s}$.

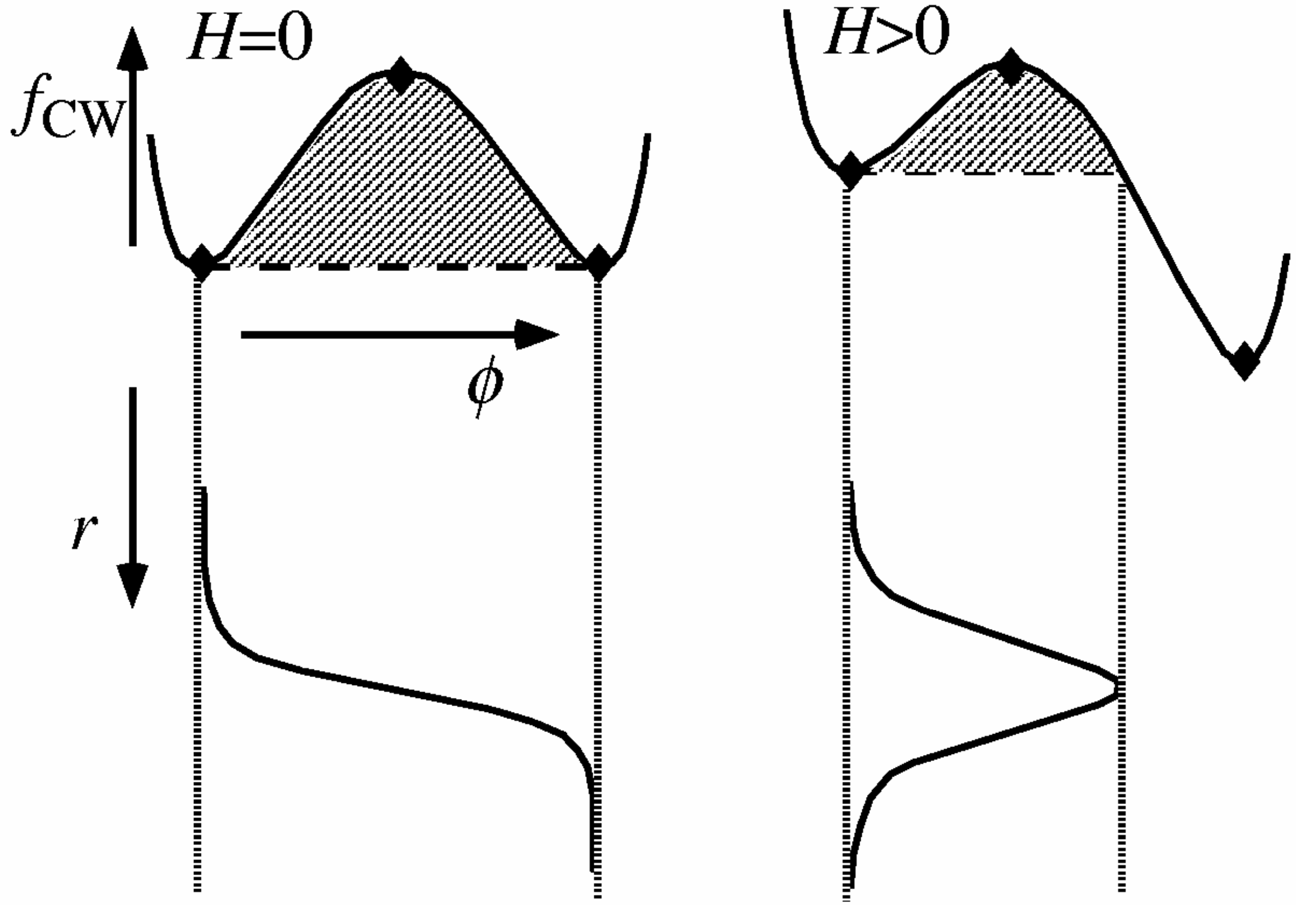
$$|\mathrm{Im}\tilde{f}| \sim \begin{cases} 0 & \text{for } |H|<|H_\mathrm{s}| \\ (|H|-|H_\mathrm{s}|)^{3/2} & \text{for } |H|>|H_\mathrm{s}| \end{cases}$$

Systems with long-range interactions

Long-Range Force system near H_s

Critical fluctuation is *ramified droplet* of size

$$\xi_r \sim (|H_s| - |H|)^{-1/4}$$



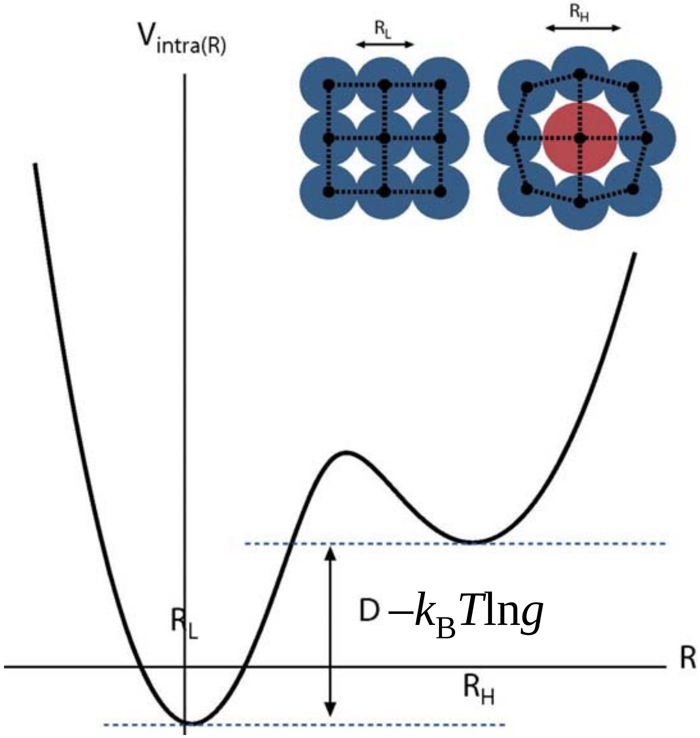
Example 1:
Spin-crossover (SC) materials with elastic interactions

- In SC materials the low-spin (LS) and high-spin (HS) molecules have different radii, $R_{HS} > R_{LS}$, and degeneracies,

  $g = g_H/g_L > 1$

- The local free energy can be expressed by effective Hamiltonian with $\sigma_i = -1$ (+1) for LS (HS)

$$\mathcal{H}_{\rm eff} = \frac{1}{2}\sum_i (D - k_{\rm B}T\ln g)\sigma_i$$



Local molecular energy

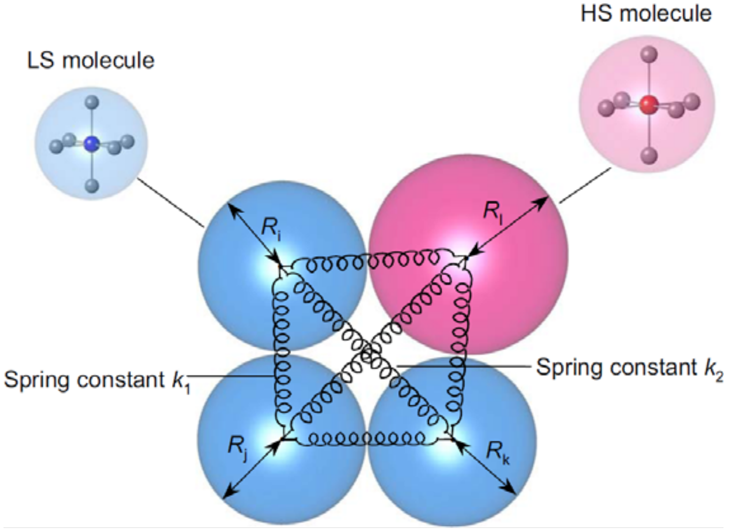
Elastic interactions

- The different molecular volumes lead to elastic interactions:

$$U = U_{\mathrm{NN}} + U_{\mathrm{NNN}}$$

with direct nearest-neighbor

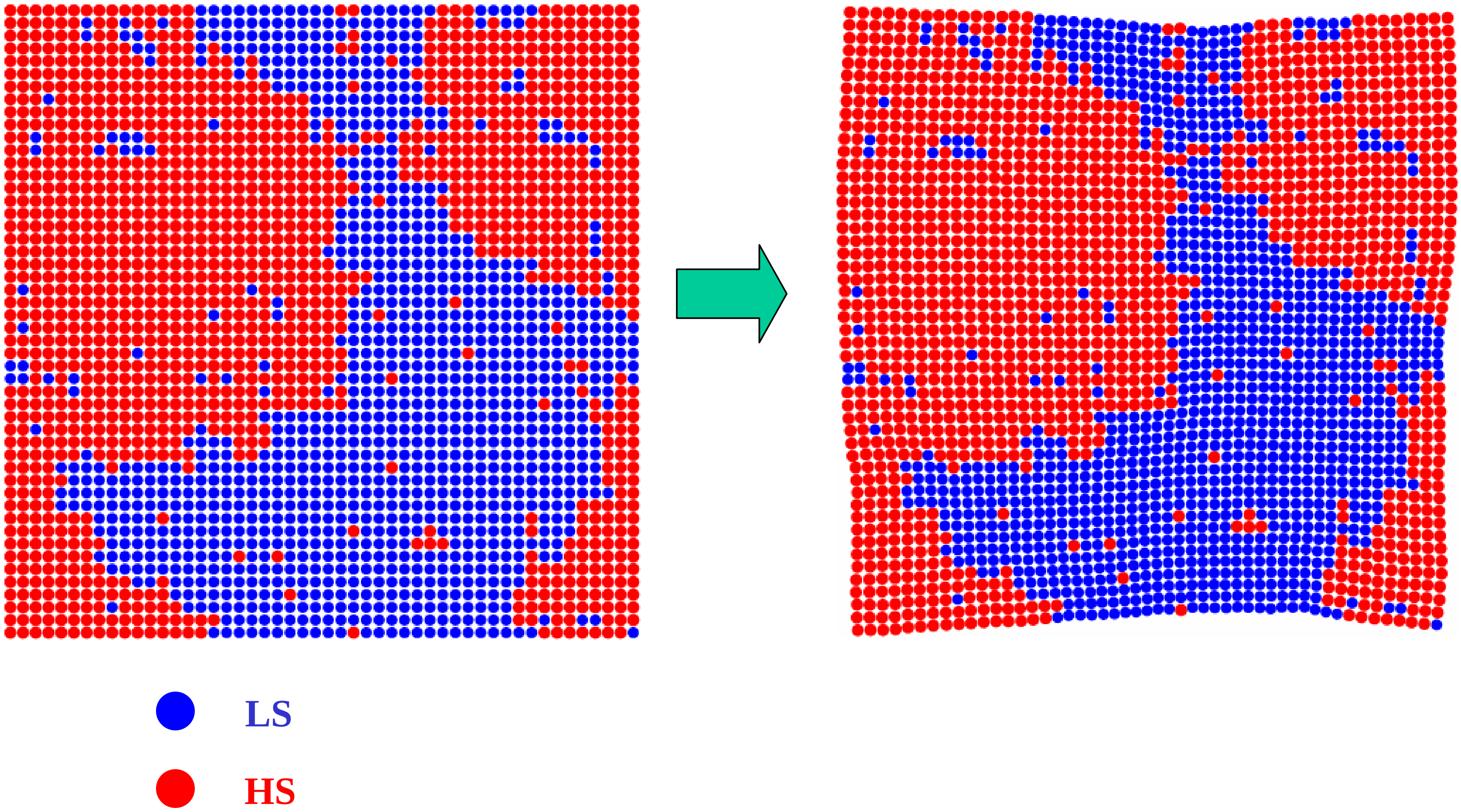
$$U_{\mathrm{NN}} = \frac{k_1}{2} \sum_{\langle i,j \rangle} [r_{ij} - (R_i + R_j)]^2$$



and next-nearest neighbor interactions

$$U_{\mathrm{NNN}} = \frac{k_2}{2} \sum_{\langle\langle i,j \rangle\rangle} [r_{ij} - \sqrt{2}(R_i + R_j)]^2$$

Distortion due to the size-difference



Order parameter

- The order parameter is the fraction of HS molecules,

$$f_{\rm HS} = \frac{1}{N}\sum_i (2\sigma_i - 1) \in [0,1]$$

- For convenience we transform this to the "magnetization"

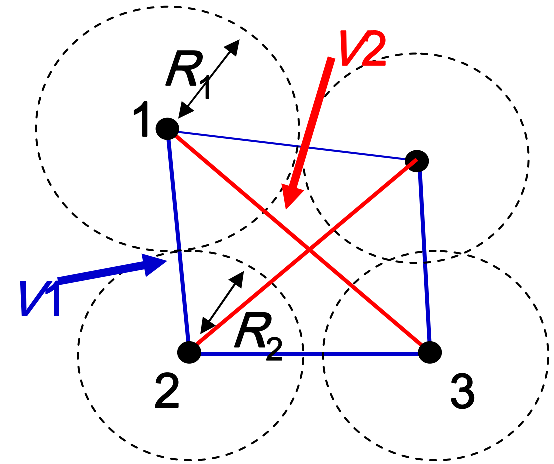
$$M = \frac{1}{2}(f_{\rm HS} - 1) \in [-1,+1]$$

NPT ensemble MC simulation

- Choose molecule n randomly
- Propose new state with prob $g/(1+g)$ for HS and $1/(1+g)$ for LS
- Propose new candidate position $\mathbf{r}_n$
- Update state and position:

$$\frac{P_{i\to k}}{P_{k\to i}} = \exp(-\beta \Delta W)$$

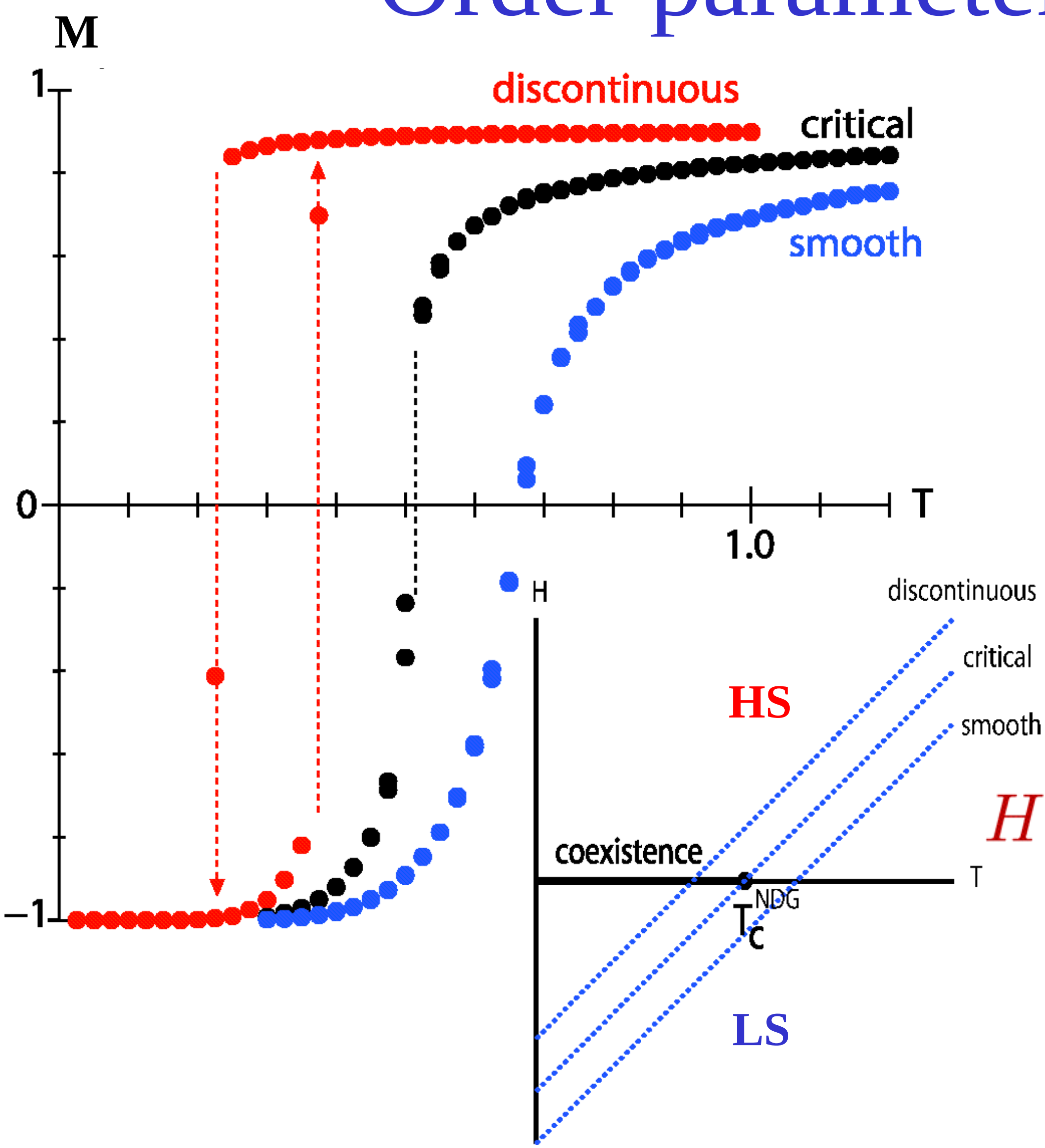
$$\Delta W = (U_k - U_i) + p(V_k - V_i) - Nk_{\mathrm{B}}T \ln\left(\frac{V_k}{V_i}\right)$$



- Repeat N times
- Choose candidate system size V
- Update V with P

Y. Konishi, H. Tokoro, M. Nishino, and S. Miyashita, PRL **100**, 067206 (2008)

Order parameter vs T

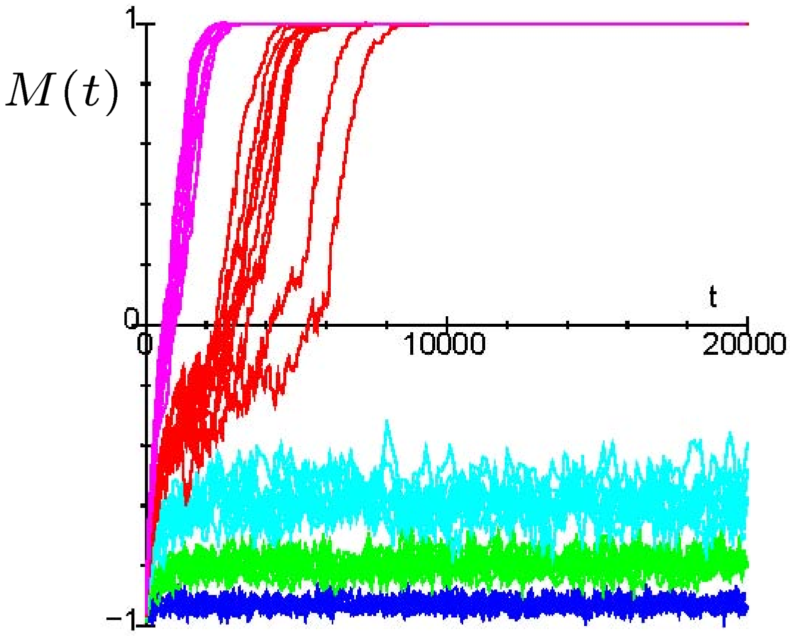


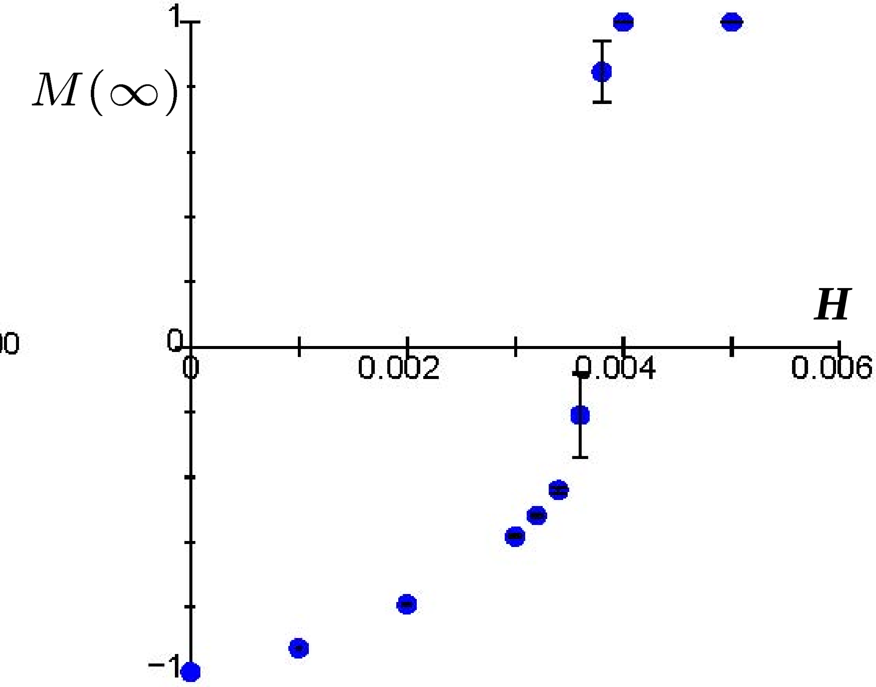
Effective field:

$$H(T) = \frac{1}{2}(D - k_{\mathrm{B}} T \ln g)$$

Dynamics under light irradiation

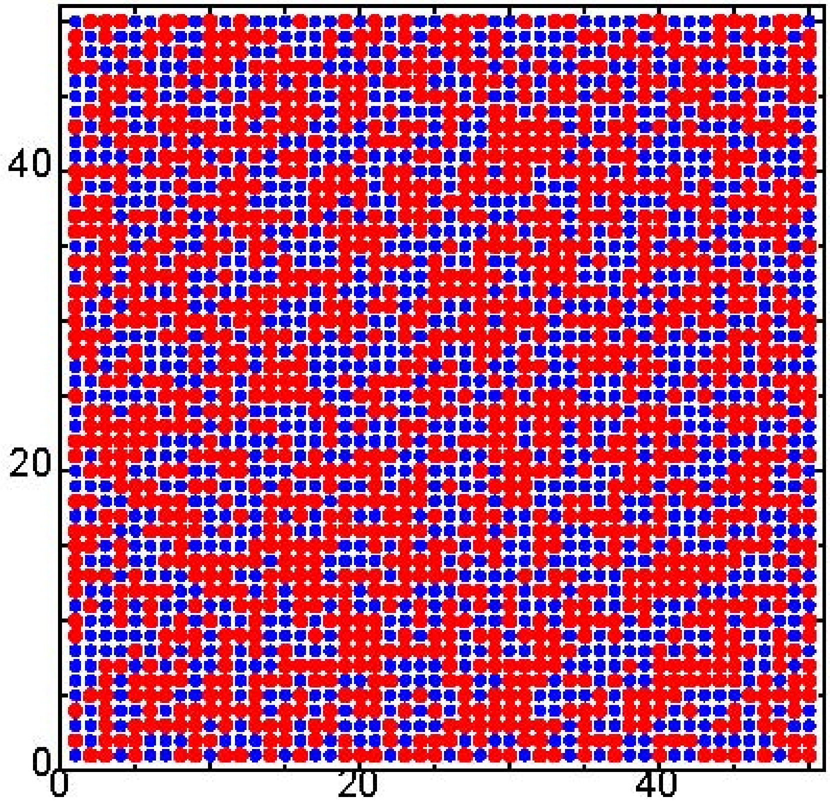
- Light irradiation will pump molecules into the HS state. Thus the light intensity acts as an **effective field** *H* in our model.

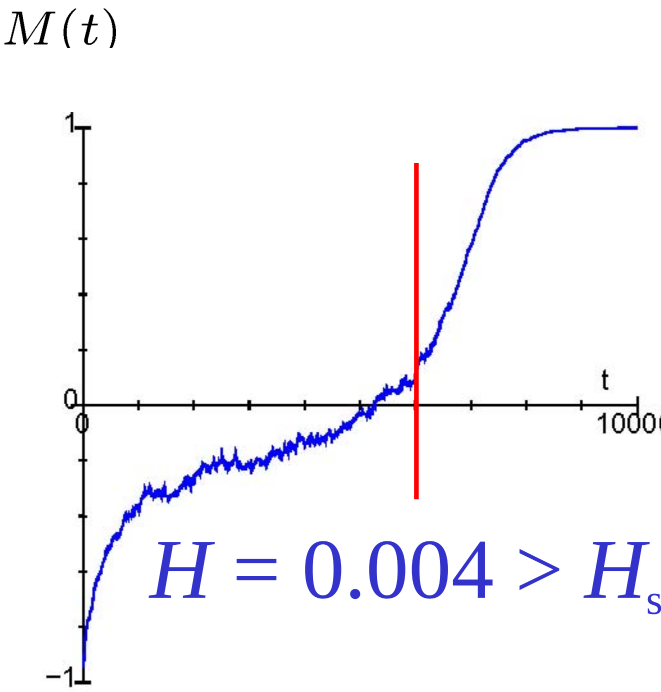




***H* = 0.001, 0.002, 0.003, 0.004, 0.005**

Ramified, growing HS cluster

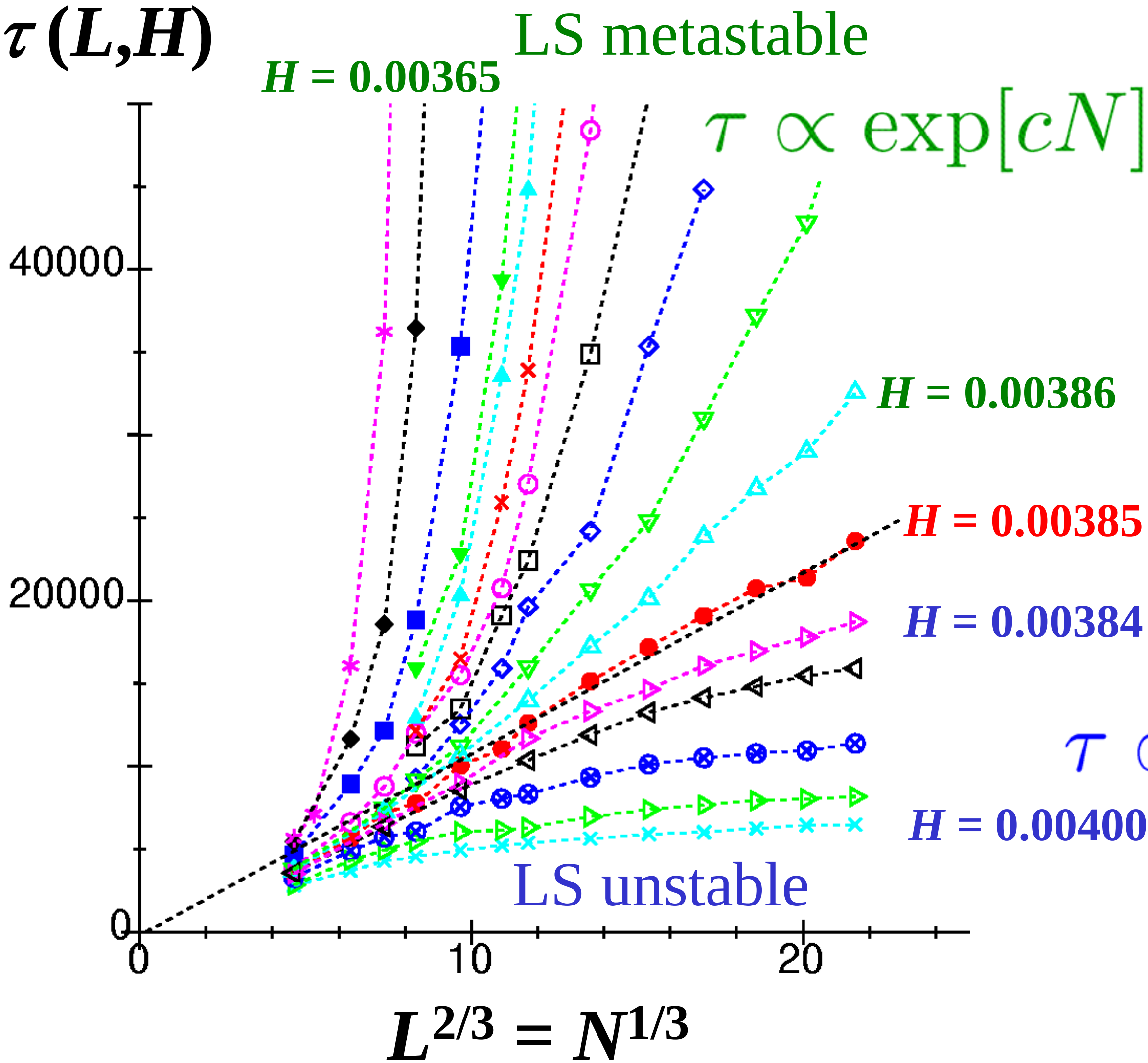




$H = 0.004 > H_{\text{spinodal}}$

Snapshot at $t = 6000$ for $H = 0.004$

Transition time vs L and H



$\tau \propto \exp[cN]$ for $H < H_{\text{spinodal}}$

$\tau \propto N^{1/3}$ for $H = H_{\text{spinodal}}$

$\tau \propto (H - H_{\text{sp}})^{-1/2}$ for $H > H_{\text{spinodal}}$

Finite-size scaling for τ

- The scaling relations in different regimes,
  - $\tau \propto \exp(cN)$ for $H < H_{sp}$ (LS metastable)
  - $\tau \propto N^{1/3}$ for $H = H_{sp}$ (spinodal point) R. Kubo, K. Matsuo, K. Kitahara, J. Stat. Phys. **9**,51 (1973).
  - $\tau \propto N^{0} (H - H_{sp})^{-1/2}$ for $H > H_{sp}$ (LS unstable) K. Binder, Phys. Rev. B **8**, 3423 (1973)

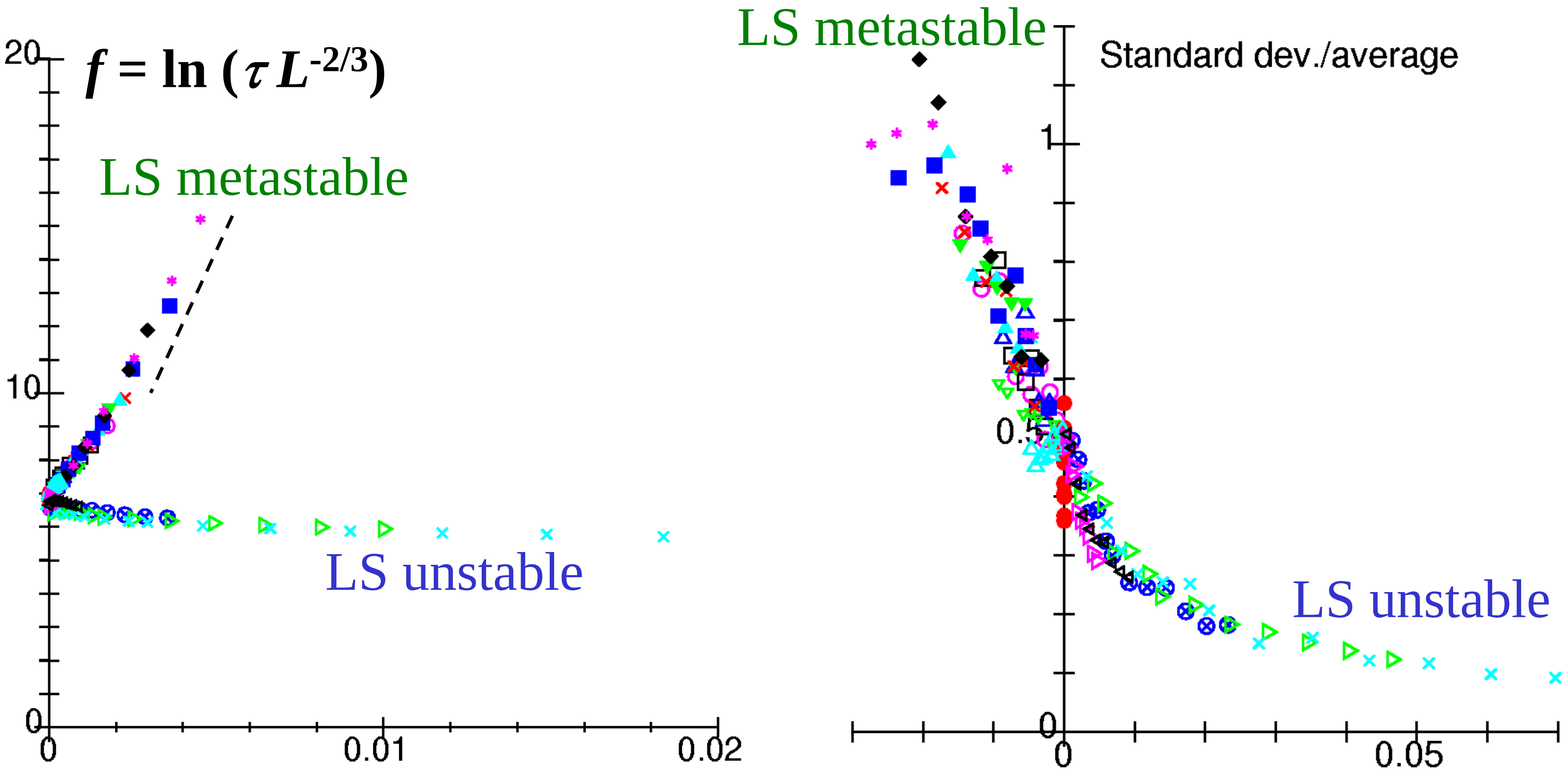
  combine into scaling form

$$\tau \propto N^{1/3} f(N^{2/3}(H - H_{sp}))$$

where f depends on $x = N^{2/3}(H - H_{sp})$ as

$$f(x) \sim \begin{cases} \exp\left(|x|^{3/2}\right) & \text{for } x \ll -1 \\ x^{0} & \text{for } |x| \ll 1 \\ x^{-1/2} & \text{for } x \gg 1 \end{cases}$$

Scaling functions (d=2)



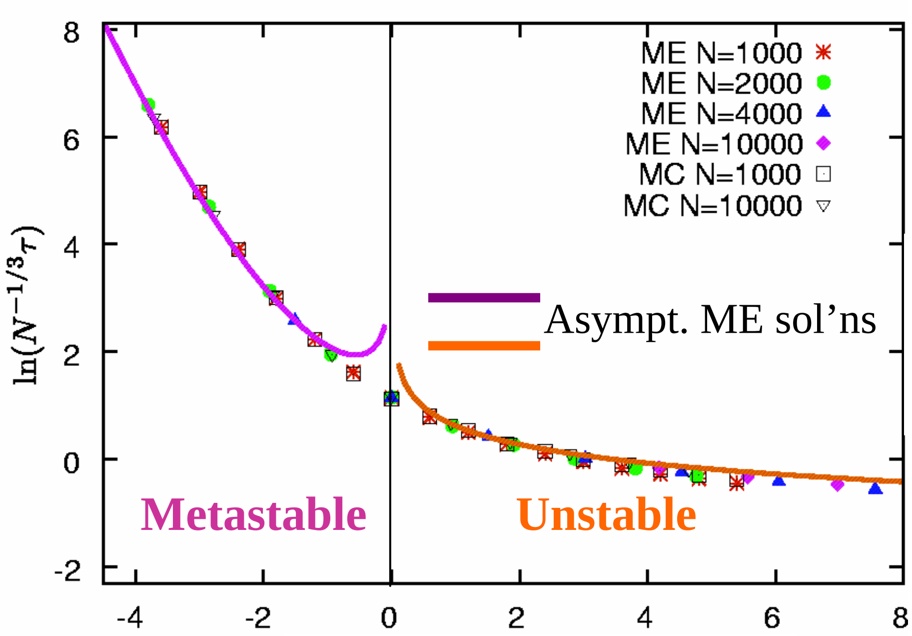
$x^{3/2} = L^2|H - H_{sp}|^{3/2}$ $\qquad$ $x = L^{4/3}(H - H_{sp})$

S. Miyashita, P. A. Rikvold, T. Mori, Y. Konishi, M. Nishino, and H. Tokoro
submitted to PRL, arXiv:0905.1161

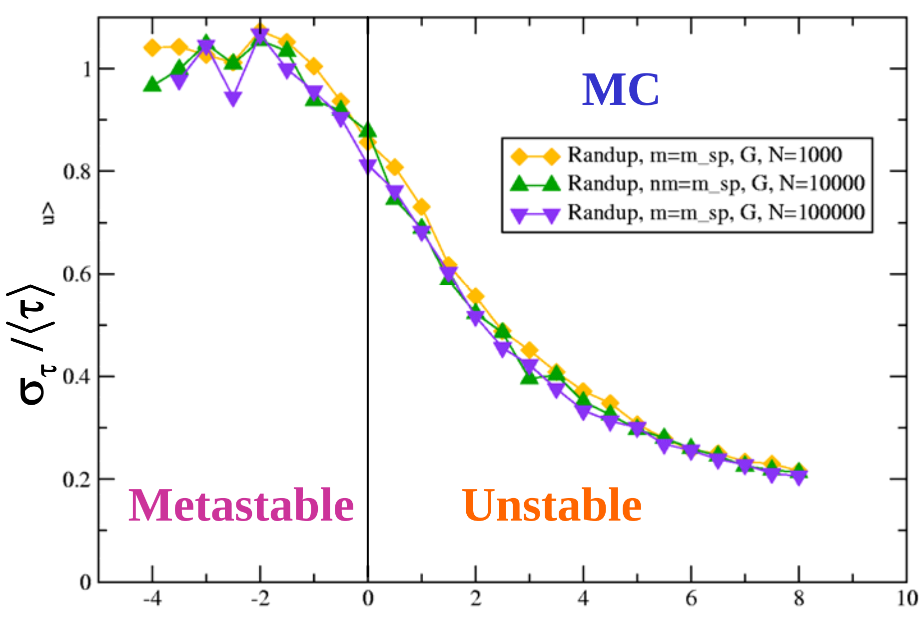
Example 2: Husimi-Temperley model

- Weak, infinitely long-range (equivalent-neighbor) model:

$$\mathcal{H} = -\frac{J}{2N} M^2 - HM, \quad M = \sum_{i=1}^{N} \sigma_i$$



$x = N^{2/3}(H - H_{sp})$



$x = N^{2/3}(H - H_{sp})$

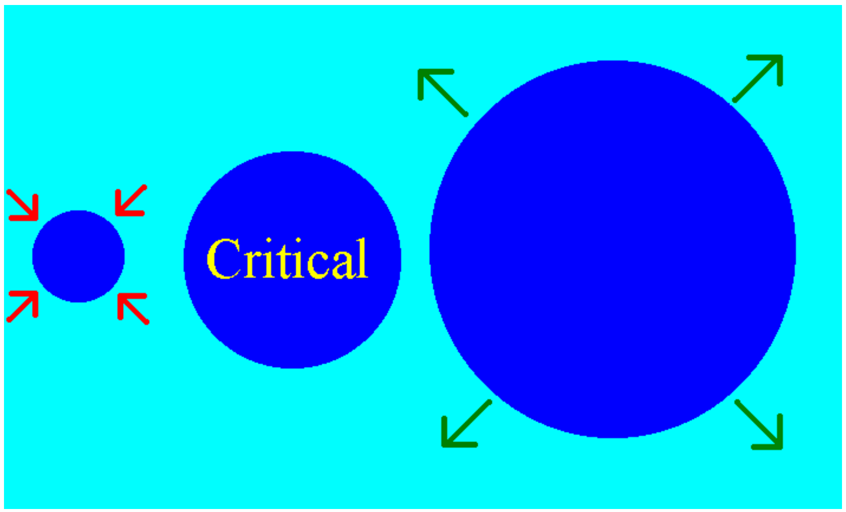
T. Mori, S. Miyashita, and P. A. Rikvold
submitted to PRE, arXiv:0905:0089

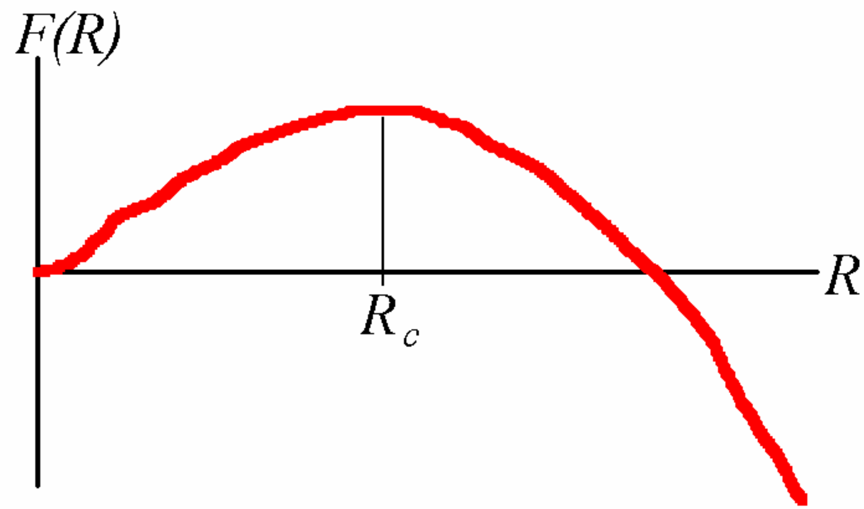
Systems with short-range interactions

Short-Range Force system

Relevant fluctuations are *compact droplets* of radius R and volume $\Omega_d R^d$ with free energy

$$F(R) \approx \Omega_d^{(d-1)/d} \sigma_0(T) R^{d-1} - |H| 2 m_{\mathrm{s}}(T) \Omega_d R^d$$





$\sigma_0(T)$: Droplet surface tension.

$m_{\mathrm{s}}(T)$: Spontaneous magnetization.

$F(R)$ is maximum for the *critical radius* $R_{\mathrm{c}} \approx \frac{(d-1)\sigma_0(T)}{2m_{\mathrm{s}}(T)|H|}$

Nucleation rate: $\Gamma(T,H) \propto |H|^K \exp\left[-\frac{\beta \Xi(T)}{|H|^{d-1}}\right]$

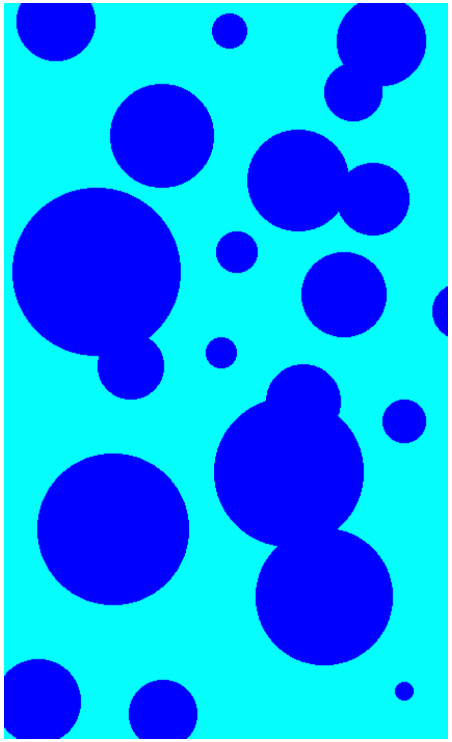
$\Xi(T)$ and K known for d=2 Ising model. *No* sharp spinodal!

Droplet Growth and Finite-Size Effects in the Ising Model

KJMA (Avrami) theory. (Kolmogorov, Johnson-Mehl, Avrami, 1939-42)

Large supercritical droplets grow at approximately constant speed (Allen-Cahn approximation):

$$\begin{aligned} v_\perp &= (d-1)\nu\left(R_c^{-1} - R^{-1}\right) \\ &\xrightarrow{R\to\infty} (d-1)\nu R_c^{-1} \equiv v_0 \propto |H| \end{aligned}$$

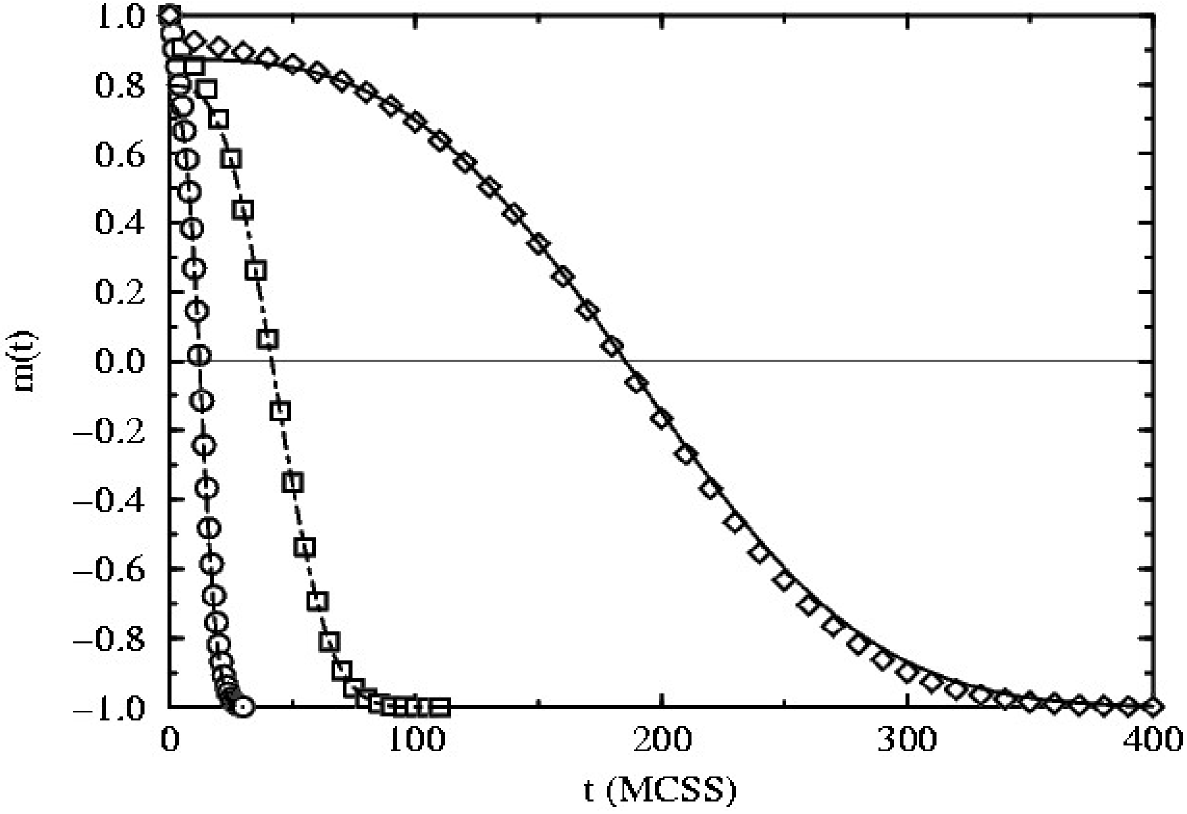


Time evolution of magnetization (randomly placed, freely overlapping droplets):

$$\begin{aligned} m(t) &\approx 2\exp\left[-\Gamma\int_0^t \Omega_d (v_0 s)^d \mathrm{d}s\right] - 1 \\ &= 2\exp\left[-\frac{\Omega_d}{d+1}\left(\frac{t}{t_0}\right)^{d+1}\right] - 1 \end{aligned}$$

where $t_0 = (v_0^d\Gamma)^{-1/(d+1)}$ is the *average time of free growth*.

KJMA magnetization



$m(t)$ vs t

$T = 0.8T_c$, $H = 0.3J$, $L = 256$

R. A. Ramos, P. A. Rikvold, and M. A. Novotny. *Phys. Rev. B* **59**, 9053-9069 (1999)

With t_0 is associated the *characteristic distance of free growth*:

$$R_0 = v_0 t_0$$

Recall nucleation rate:

$$\Gamma = \frac{\beta\kappa}{\pi}|\mathrm{Im}\tilde{f}| \propto |H|^K \exp\left[-\frac{\beta\Xi(T)}{|H|^{d-1}}\right]$$

Using this, we have:

$$t_0(T,H) \propto \exp\left[\frac{1}{d+1}\frac{\beta\Xi(T)}{|H|^{d-1}}\right]$$

and

$$R_0(T,H) \propto \exp\left[\frac{1}{d+1}\frac{\beta\Xi(T)}{|H|^{d-1}}\right]$$

Finite-Size Effects

Hypercube of side L. Compare L, R_0 and R_c.

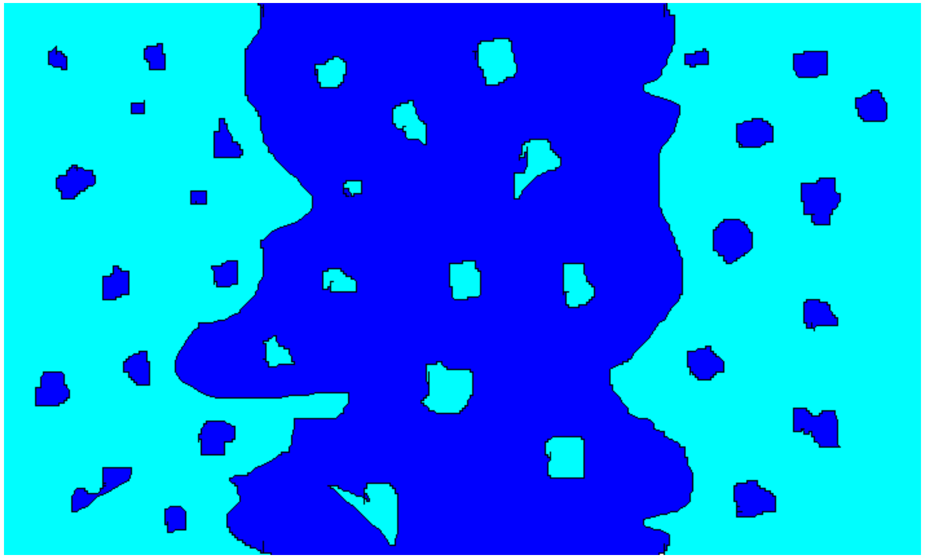
Average metastable lifetime: τ

Small-L: $R_0 \gg R_c \gg L$

No critical droplet (*Coexistence Regime*).

Decay caused by *subcritical* fluctuation.

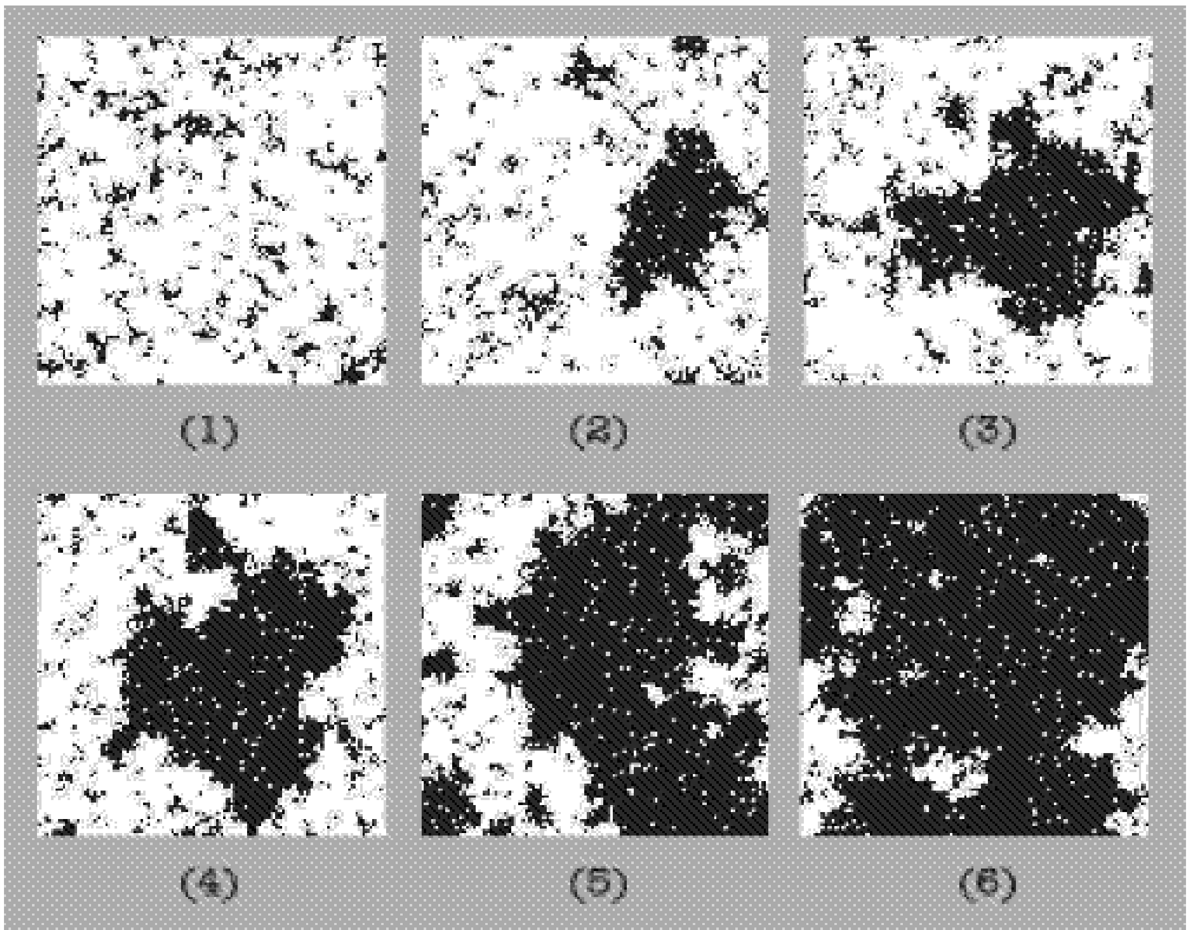
$$\tau \propto \exp\left[L^{d-1}\right]$$



Intermediate-L: $R_0 \gg L \gg R_c$

One growing droplet (*Single-Droplet Regime*).

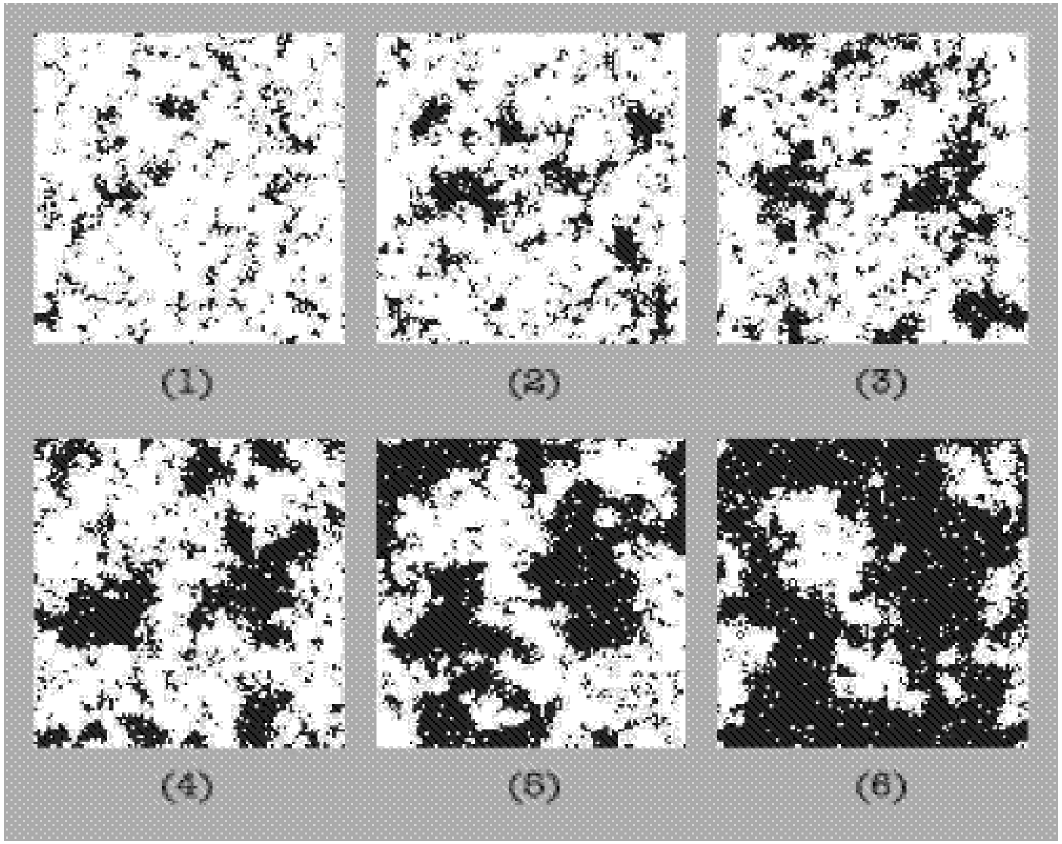
$$\tau \propto (L^d \Gamma)^{-1} \propto L^{-d} \exp\left[\frac{\beta \Xi(T)}{|H|^{d-1}}\right]$$



Large-L: $L \gg R_0 \gg R_c$

Many growing droplets (*Multi-Droplet Regime*).

$$\tau \propto t_0 \propto \exp\left[\frac{1}{d+1}\,\frac{\beta\Xi(T)}{|H|^{d-1}}\right]$$



Crossover Fields

$R_0 \approx L$ *Dynamic Spinodal* (DSP)

$$H_{\mathrm{DSP}} \approx \left(\frac{1}{d+1} \, \frac{\beta \Xi(T)}{\ln L} \right)^{\frac{1}{d-1}}$$

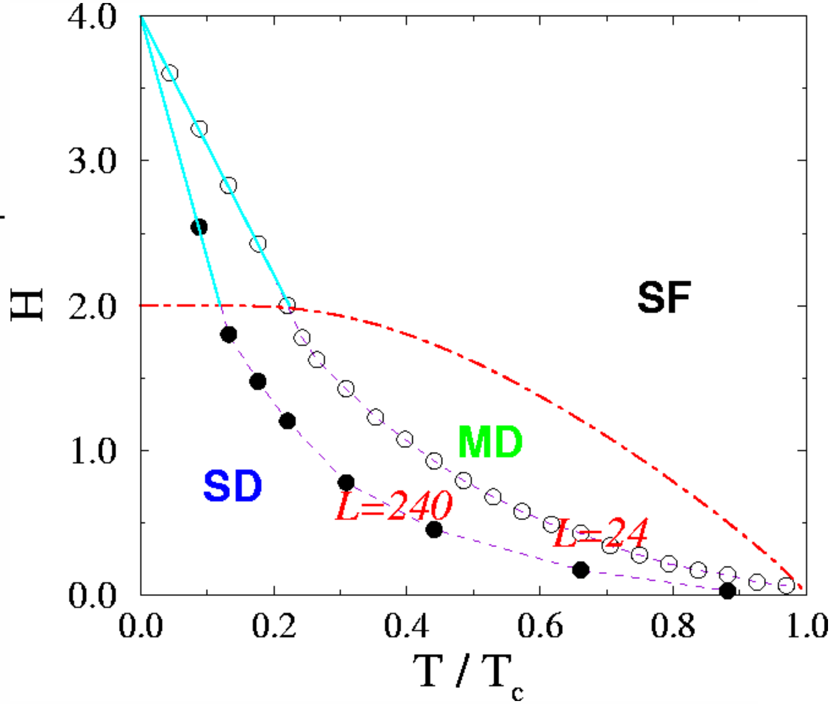
EXCEEDINGLY SLOW CONVERGENCE WITH L !!!

$R_c \approx L$ *Thermodynamic Spinodal* (THSP)

$$H_{\mathrm{THSP}} \propto \frac{1}{L} \, \frac{(d-1)\sigma_0(T)}{m_{\mathrm{s}}(T)}$$

$R_c \approx 1/2$ *Mean-field Spinodal* (MFSP)

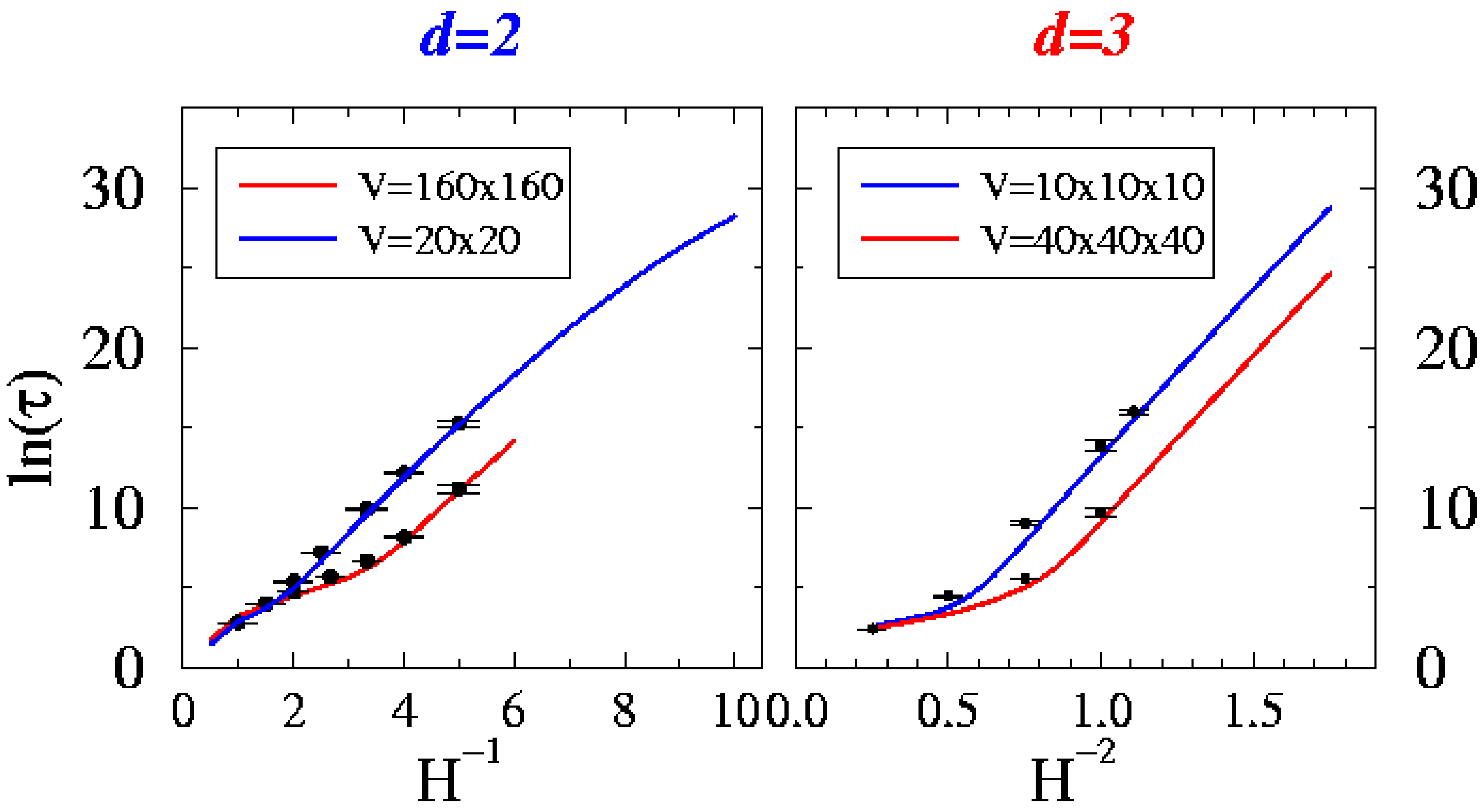
$$H_{\mathrm{MFSP}} \approx \sigma_0(T)/m(T)$$



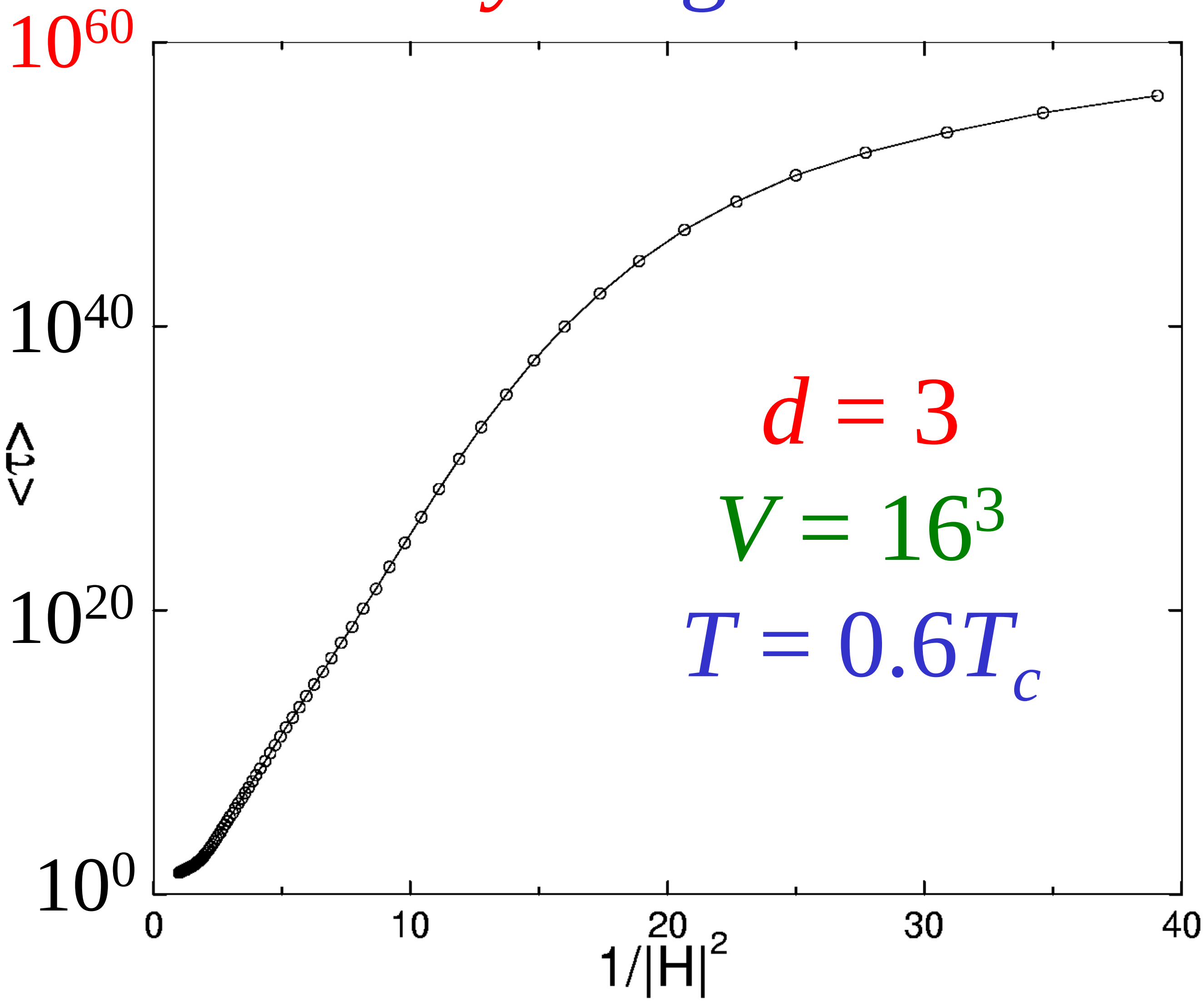
Metastable phase diagram

P. A. Rikvold, H. Tomita, S. Miyashita, S. W. Sides, *Phys. Rev. E* **49**, 5080-5090 (1994)

Lifetime vs $H^{-(dimension-1)}$



Really long times



Projected dynamics simulation

M. Kolesik, M. A. Novotny, and P. A. Rikvold. *Int. J. Mod. Phys. C* **14**, 121-132 (2003)

Points to remember

- Metastability common in wide variety of physical and chemical systems: diamonds, magnets, ferroelectrics, supercooled and supersaturated fluids, quark-gluon plasma, …
- "Toy models" enable us to study various decay mechanisms
- The interplay of nucleation and growth essential
- *Only* mean-field and long-range force systems have sharp spinodal
- Short-range force systems have size-dependent "spinodals"

Remaining lectures:

2. Dynamics of magnetization switching in models of magnetic nanoparticles and ultrathin films
3. Hysteresis and dynamic phase transition in kinetic Ising models and ultrathin magnetic films

The ice storm of 1998. Ottawa

Photo: Michael J. Thompson http://www.playground.net/~thompson/