Statistical Mechanics of Ising model – brief course

Thermodynamics and Statistical Mechanics (I)

Equilibrium + canonical ensemble

Probability that the system is in state μ is

$$P_\mu = \frac{1}{\mathcal{Z}} e^{-\beta \mathcal{H}_\mu}$$

Partition function

$$\mathcal{Z} = \sum_\mu e^{-\beta \mathcal{H}_\mu}$$

Temperature T and $\beta = 1/k_B T$

Observables:

1. Free Energy
$$F = -k_B T \log \mathcal{Z}$$
2. Internal Energy
$$U = \langle \mathcal{H} \rangle = \frac{1}{\mathcal{Z}} \sum_\mu \mathcal{H}_\mu e^{-\beta \mathcal{H}_\mu} = -\frac{\partial \log \mathcal{Z}}{\partial \beta}$$
3. Entropy
$$S = \frac{U - F}{T} = -\frac{\partial F}{\partial T}$$
4. Order parameter
$$M = \langle m \rangle = \frac{1}{\mathcal{Z}} \sum_\mu m_\mu e^{-\beta \mathcal{H}_\mu(m)} = -\frac{\partial F}{\partial h}$$

Thermodynamics and Statistical Mechanics (II)

Fluctuations & Correlations:

1. Specific heat

$$k_B T^2 C_V = \langle \mathcal{H}^2 \rangle - \langle \mathcal{H} \rangle^2 = \frac{\partial^2 \log \mathcal{Z}}{\partial \beta^2}$$

$$C_V = -T \frac{\partial^2 F}{\partial T^2}$$

2. Susceptibility

$$k_B T \chi_M = \langle m^2 \rangle - \langle m \rangle^2 = -k_B T \frac{\partial^2 F}{\partial h^2}$$

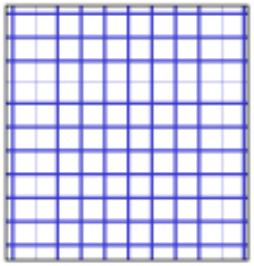
3. Correlation functions

$$G_c^{(2)}(i,j) = \langle m_i m_j \rangle - \langle m_i \rangle \langle m_j \rangle = -k_B T \frac{\partial^2 F}{\partial h_i \partial h_j}$$

Notice:

- Observables : first derivatives
- Fluctuations & Correlations : second derivatives

The Model

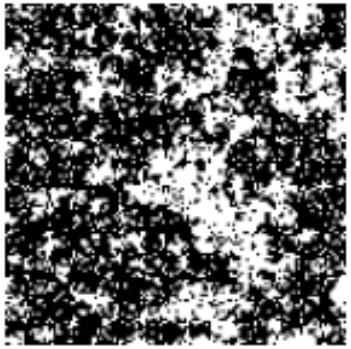


- Consider a lattice with L^2 sites and their connectivity (e.g. a square lattice).
- Each lattice site has a single spin variable: $s_i = \pm 1$.
- With magnetic field **h**, the energy is:

$$H = -\sum_{(i,j)} J_{ij} s_i s_j - \sum_{i=1}^{N} h_i s_i \qquad and \quad Z = \sum e^{-\beta H}$$

- J is the nearest neighbors (i,j) coupling:
  - J > 0 ferromagnetic.
  - J < 0 antiferromagnetic.

- Picture of spins at the critical temperature T_c. (Note that connected (percolated) clusters.)



Brief History

Lenz (1888-1957): Proposed a model of ferromagnetism.

Ising (1900-1998): Solved the 1D Model during his PhD (1924).

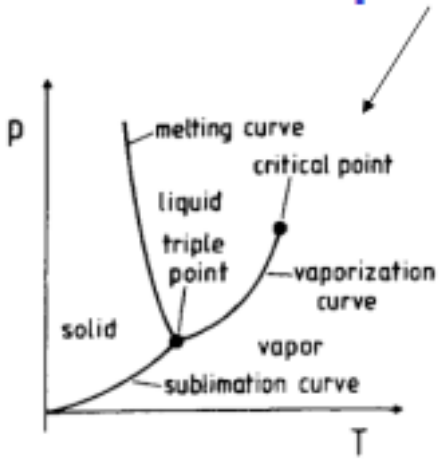
Onsager (1903-1976): Solved the 2D Model (1944).

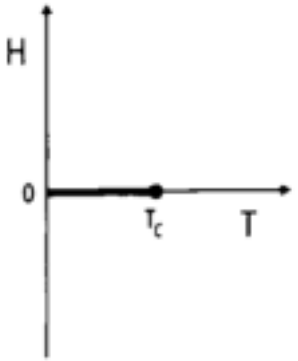
Zamolodchikov: Solved the 2D Model with magnetic field (1989).

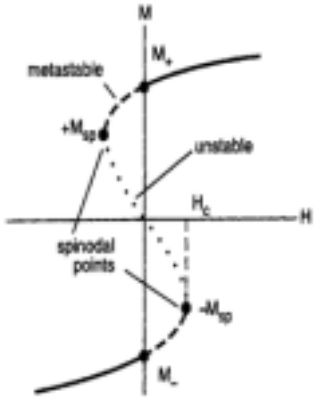
?: 3D still unsolved (NP problem).

Phase Diagram

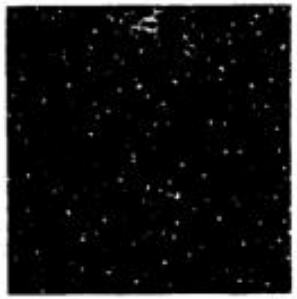
- **High-T phase:** spins are random (uncorrelated).
- **$T > T_c$ phase near T_c:** spins are random but correlated: magnetic short-range (local) order.
- **Low-T (T~0) phase:** spins are aligned (fully correlated).
- A ***first-order transition*** (where there is a discontinuous jump in **M**) occurs as H passes through zero for $T<T_c$.
- Similar to **LJ phase diagram**. Magnetic field=pressure.



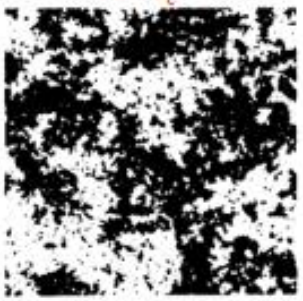




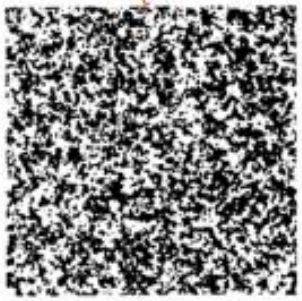
Low T



$T \sim T_c$



$T >> T_c$



Markov Process

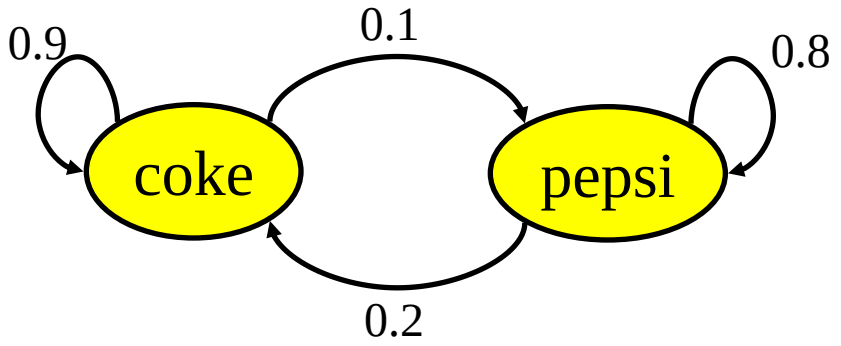
Coke vs. Pepsi Example

- Given that a person's last cola purchase was Coke, there is a 90% chance that his next cola purchase will also be Coke.

- If a person's last cola purchase was Pepsi, there is an 80% chance that his next cola purchase will also be Pepsi.

transition matrix:

$$P = \begin{bmatrix} 0.9 & 0.1 \\ 0.2 & 0.8 \end{bmatrix}$$



Markov Process

Coke vs. Pepsi Example (cont)

Given that a person is currently a Pepsi purchaser, what is the probability that he will purchase Coke two purchases from now?

Pr[Pepsi→?→Coke] =

Pr[Pepsi→Coke→Coke] + Pr[Pepsi→ Pepsi →Coke] =

0.2 * 0.9 + 0.8 * 0.2 = 0.34

$$P = \begin{bmatrix} 0.9 & 0.1 \\ 0.2 & 0.8 \end{bmatrix} \begin{bmatrix} 0.9 & 0.1 \\ 0.2 & 0.8 \end{bmatrix} = \begin{bmatrix} 0.83 & 0.17 \\ 0.34 & 0.66 \end{bmatrix}$$

Pepsi → ? ? → Coke

Markov Process

Coke vs. Pepsi Example (cont)

Given that a person is currently a Coke purchaser, what is the probability that he will purchase Pepsi **three** purchases from now?

$$P^3 = \begin{bmatrix} 0.9 & 0.1 \\ 0.2 & 0.8 \end{bmatrix} \begin{bmatrix} 0.83 & 0.17 \\ 0.34 & 0.66 \end{bmatrix} = \begin{bmatrix} 0.781 & 0.219 \\ 0.438 & 0.562 \end{bmatrix}$$

Markov Process

Coke vs. Pepsi Example (cont)

- Assume each person makes one cola purchase per week
- Suppose 60% of all people now drink Coke, and 40% drink Pepsi
- What fraction of people will be drinking Coke three weeks from now?

$$P = \begin{bmatrix} 0.9 & 0.1 \\ 0.2 & 0.8 \end{bmatrix} \qquad P^3 = \begin{bmatrix} 0.781 & 0.219 \\ 0.438 & 0.562 \end{bmatrix}$$

$$\Pr[X_3 = \text{Coke}] = 0.6 * 0.781 + 0.4 * 0.438 = 0.6438$$

Q_i - the distribution in week i

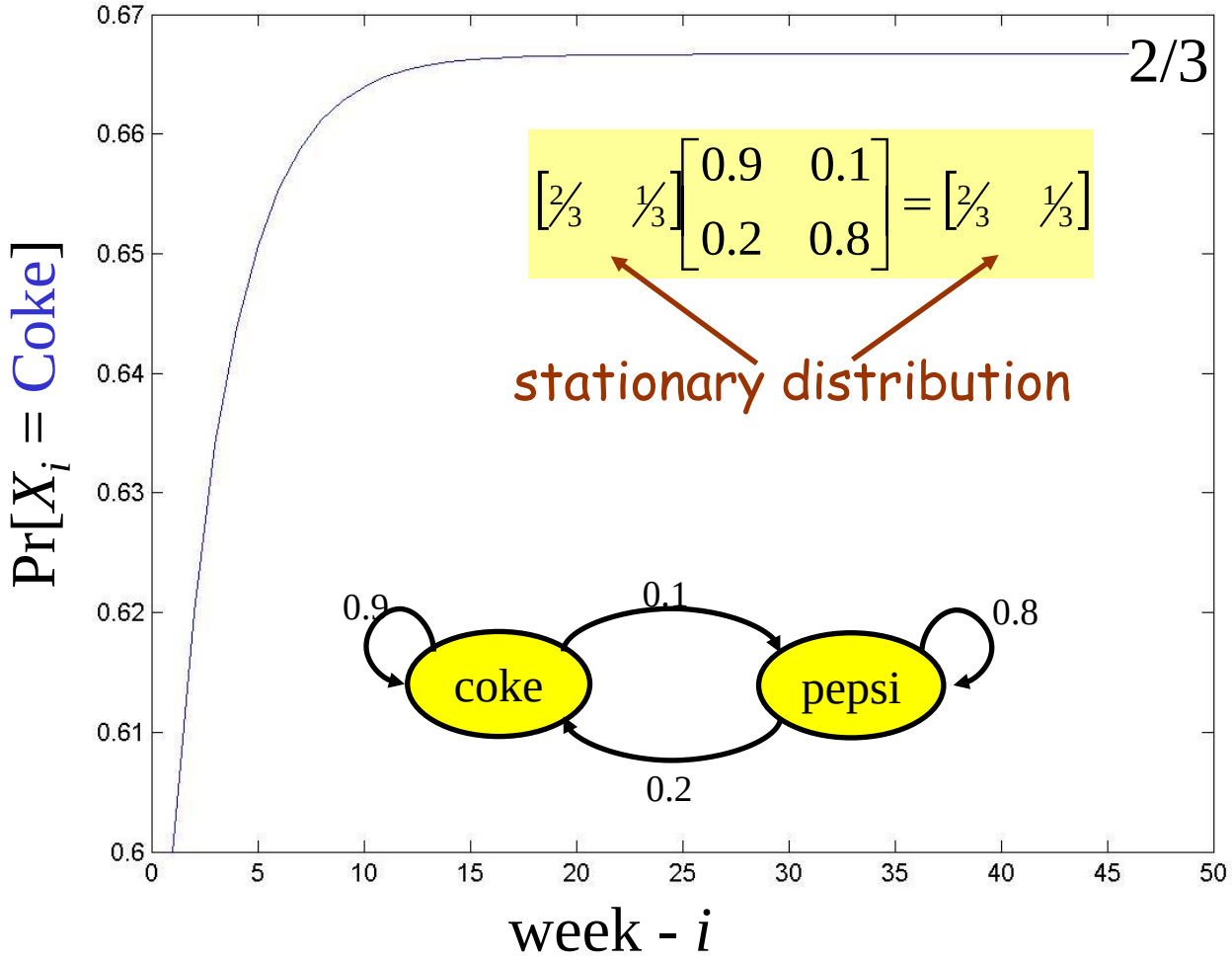
$Q_0 = (0.6, 0.4)$ - initial distribution

$Q_3 = Q_0 * P^3 = (0.6438, 0.3562)$

Markov Process

Coke vs. Pepsi Example (cont)

Simulation:



Markov Chain Monte Carlo

- Generate a sequence of states $X_0, X_1, \ldots, X_n$, such that the limiting (stationary) distribution is given P(X)
- Move X by the transition probability

  W(X -> X')
- Starting from arbitrary $P_0(X)$, we have

  $P_{n+1}(X) = \sum_{X'} P_n(X') W(X' \rightarrow X)$
- $P_n(X)$ approaches P(X) as *n* go to ∞

Necessary and sufficient conditions for convergence

- Ergodicity

  $[W^n](X \rightarrow X') > 0$

  For all $n > n_{max}$, all X and X'

- Detailed Balance

  $P(X)\, W(X \rightarrow X') = P(X')\, W(X' \rightarrow X)$

Taking Statistics

- After equilibration, we estimate:

$$\langle Q(X) \rangle = \int Q(X) P(X) \, \mathrm{d}X \approx \frac{1}{N} \sum_{i=1}^{N} Q(X_i)$$

where X_i are generated by the stochastic process (Markov chain).

Remark: probability distribution P(X) is „absorbed” in the stochastic process that generate X_i.

Choice of Transition Matrix W

- The choice of W determines an algorithm. The equation

  $$P(X)W(X->X')=P(X')W(X'->X)$$

  has (infinitely) many solutions given P.
- Any one of them can be used for Monte Carlo simulation. One of the simplest and most popular is the so-called Metropolis algorithm.

Metropolis importance sampling Monte Carlo scheme

(1) Choose an initial state
(2) Choose a site i
(3) Calculate the energy change ΔE which results if the spin at site i is overturned
(4) Generate a random number r such that $0 < r < 1$
(5) If $r < \exp(-\Delta E/k_B T)$, flip the spin
(6) Go the next site and go to (3)

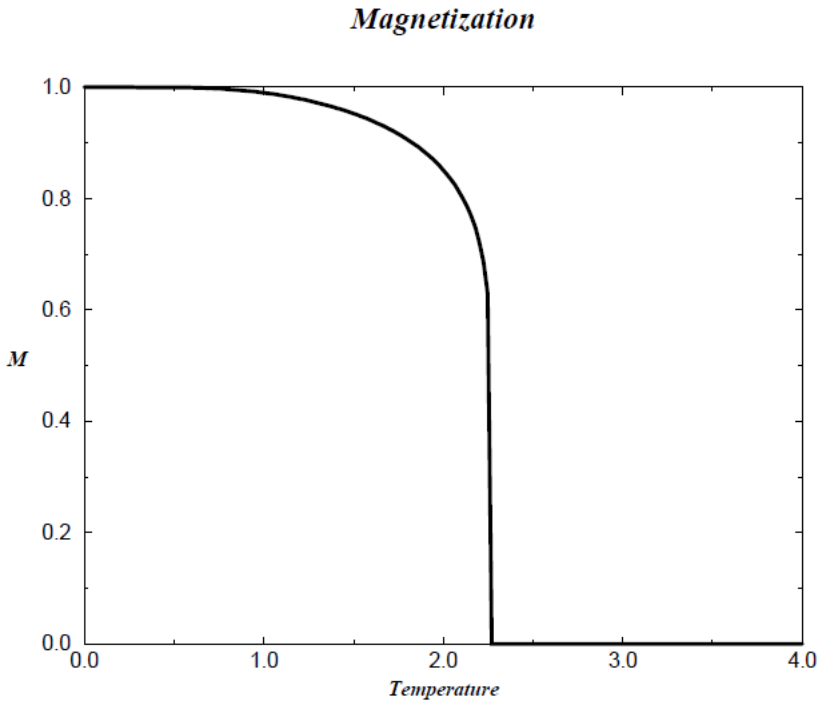
Ferromagnetic Phase Transition

Second Order Phase Transition.

Magnetization : Order Parameter.

Low Temperature : Ferromagnetic Phase ($M \neq 0$).

High Temperature : Paramgnetic Phase ($M = 0$).



Thermodynamical Quantities (I)

Average quantities:

$$\langle Q \rangle = \frac{\sum_\mu Q_\mu e^{-\beta E_\mu}}{\sum_\mu e^{-\beta E_\mu}}$$

Magnetization:

$$M = \frac{1}{N} \sum_{i=1}^{N} S_i$$

Energy:

$$E = -\frac{J}{N} \sum_{<i,j>} S_i S_j$$

Fluctuations:

Susceptibility:

$$\chi \equiv \frac{1}{N} \left. \frac{\partial \langle M \rangle}{\partial h} \right|_{h=0} = \frac{\beta}{N} \left(\langle M^2 \rangle - \langle M \rangle^2 \right)$$

Specific heat:

$$C \equiv \frac{\partial \langle E \rangle}{\partial T} = k\beta^2 \left(\langle E^2 \rangle - \langle E \rangle^2 \right)$$

Thermodynamical Quantities (II)

Entropy:

$$S = \int_0^T \frac{\partial S}{\partial T} dT = \int_0^T \frac{C}{T} dT$$

Partition function:

$$Z = \exp(-\beta F) = \exp\left(S - \beta \langle E \rangle\right)$$

Connected Correlation Fucntion:

$$G_c^{(2)}(i,j) = \quad < S_i S_j > - < S_i > < S_j > = < S_i S_j > - \mathrm{m}^2$$

Correlation length:

$$G(r) \sim \exp(-r/\xi)$$

Time displaced correlation:

$$\chi(t) = \int [m(t'+t)m(t') - m^2] dt'$$

Correlation time:

$$\chi(t) \sim \exp(-t/\tau).$$

Spontaneous symmetry breaking in Ising model (h=0)

Hamiltonian preserves (global) up-down symmetry

Magnetization should be thus always zero

In the limit of large system (and sufficiently low temperature) the ergodicity is broken and time average does not equal to the canonical average

Mean-field approximation

In the mean-field approximation we consider a single spin. Its interactions with other spins are replaced by a certain effective (mean) field:

$$\epsilon_{mf}(S_j) = -hS_j - JS_j \sum_{k}^{n.n} \langle S_k \rangle = -h_{mf} S_j$$

where

$$h_{mf} = h + Jzm$$

and m, the magnetisation per spin, is just the mean value of any given spin

$$m = \frac{1}{N} \sum_i \langle S_i \rangle = \langle S_k \rangle \quad \forall k$$

z – number of nearest neighbours

Mean-field approximation

Thus, the Ising model becomes equivalent to the system of noninteracting spins in the effective field. For each such a spin the Boltzmann probability becomes:

$$p(S_j) = \frac{\mathrm{e}^{-\beta\epsilon_{mf}(S_j)}}{\sum_{S_j=\pm1}\mathrm{e}^{-\beta\epsilon_{mf}(S_j)}} = \frac{\mathrm{e}^{\beta h_{mf}S_j}}{\mathrm{e}^{\beta h_{mf}} + \mathrm{e}^{-\beta h_{mf}}}$$

For such a spin one can calculate its magnetization:

$$\begin{aligned} m &= \sum_{S_j=\pm1} p(S_j)S_j \\ &= \frac{\mathrm{e}^{\beta h_{mf}} - \mathrm{e}^{-\beta h_{mf}}}{\mathrm{e}^{\beta h_{mf}} + \mathrm{e}^{-\beta h_{mf}}} = \tanh(\beta h_{mf}) \end{aligned}$$

Mean-field approximation

Thus one arrives at the following equation:

$$\boxed{m = \tanh(\beta h + \beta J z m)}$$

Problem: Find the critical temperature T_c within MFA and magnetzation close to T_c.

Using $$\tanh x \simeq x - \frac{x^3}{3}$$

one finds that m=0 is the only solution for T> T_c, where $T_c = \frac{zJ}{k}$

Near T_c one obtains: $$m = m\frac{T_c}{T} - \frac{m^3}{3}\left(\frac{T_c}{T}\right)^3$$

And thus: $$m^2 = 3\left(\frac{T}{T_c}\right)^3\left(\frac{T_c}{T} - 1\right)$$

Mean-field approximation

Introducing the reduced temperature $\boxed{t = \dfrac{T - T_c}{T_c}}$

One arrives at:

$$\boxed{\begin{array}{ll} T > T_c & m = 0 \\ T < T_c & m \simeq \pm(3|t|)^{1/2} \end{array}}$$

Problem: Find the susceptibility $\chi = \left.\dfrac{\partial m}{\partial h}\right|_{h=0}$

Expanding mean-field equation in presence of magnetic field h one finds

$$m = m\frac{T_c}{T} + \beta h - \frac{m^3}{3}\left(\frac{T_c}{T}\right)^3$$

That after differentiation gives

$$\chi = \chi\frac{T_c}{T} + \beta - \chi m^2\left(\frac{T_c}{T}\right)^3$$

Mean-field approximation

Finally one obtains:

$$T > T_c \qquad \chi = \frac{\beta}{\left(1 - \frac{T_c}{T}\right)} \simeq \frac{\beta}{t}$$

$$T < T_c \qquad \chi = \frac{\beta}{\left(1 - \frac{T_c}{T} + 3\left(\frac{T_c}{T} - 1\right)\right)} \simeq \frac{\beta}{2|t|}$$

Problem: Calculate susceptibility using the exact identity

$$\chi = \frac{\partial m}{\partial h} = \frac{\beta}{N} \sum_{jk} [\langle S_j S_k \rangle - \langle S_j \rangle \langle S_k \rangle]$$

Within MFA one obtains: $\chi = \frac{\beta}{N} \sum_{j} \left[\langle S_j^2 \rangle - \langle S_j \rangle^2 \right] = \beta [1 - m^2]$

That does not diverge at the critical temperature. (MFA is inconsistent!)

Mean-field approximation - free energy approach

In the mean-field approximation the mean Ising energy becomes

$$\begin{aligned} \overline{E} &= -h\sum_{i=1}^{N}\langle S_i\rangle - J\sum_{\langle ij\rangle}\langle S_i S_j\rangle \\ &\simeq -hNm - \frac{JzN}{2}m^2 \end{aligned}$$

Assuming that c is the mean-field probability of a spin being „up” we have:

$$m = \langle S_i\rangle = c - (1-c)$$

and

$$c = \frac{m+1}{2}$$

Mean-field approximation - free energy approach

This gives the Gibbs entropy of an assembly of N spins as

$$S = -Nk\left[c\ln c + (1-c)\ln(1-c)\right]$$

The Helmholtz free energy as a function of m is then

$$F(m) = E(m) - TS(m)$$

and the free energy per spin is given by

$$f(m) = \frac{F(m)}{N} = -\frac{Jzm^2}{2} - hm + kT\left[c\ln c + (1-c)\ln(1-c)\right]$$

To find the equilibrium state we should minimise F or f with respect to m.

Finally, one obtains

$$m = \tanh\beta(Jzm + h)$$

To summarise, the procedure is to approximate the free energy (in this case by using a non-interacting, mean-field energy) as a function of the order parameter, then minimise.

Mean-field approximation - free energy approach

It is illuminating to plot the free energy as a function of m for different T. Let us take $h = 0$

$$\frac{f(m)}{kT} = -\frac{T_c}{T}\frac{m^2}{2} + \left[\left(\frac{1+m}{2}\right)\ln\left(\frac{1+m}{2}\right) + \left(\frac{1-m}{2}\right)\ln\left(\frac{1-m}{2}\right)\right]$$

- Note that $f(m)$ is symmetric in m i.e. $f(m) = f(-m)$
- For $T > T_c$ there is a single minimum at $m = 0$ which is the equilibrium state
- At the critical point

$$\left.\frac{\partial^2 f}{\partial m^2}\right|_{m=0} = 0 \quad \text{at} \quad T = T_c$$

- For $T < T_c$ two symmetric minima emerge and $m = 0$ becomes a maximum, thus is unstable.
- For $T < T_c$ the symmetry $m \to -m$ is *spontaneously broken* since the system must select one of the two minima for its equilibrium state.

Mean-field approximation - free energy approach

Problem: Show that the mean-field free energy can be expanded as

$$\frac{f(m)}{kT} = \frac{m^2}{2}\left(\frac{T - T_c}{T}\right) + \frac{m^4}{12} + O(m^6)$$

Problem: Examine the free energy in presence of magnetic field.

Universality and Critical Exponents

Reduced temperature : $\Delta T = (T - T_c)/T_c$

$$
\begin{aligned}
C &\sim |\Delta T|^{-\alpha} \\
\langle M \rangle &\sim |\Delta T|^{\beta} \quad \text{for } \Delta T < 0 \\
\chi &\sim |\Delta T|^{-\gamma} \\
\langle M \rangle &\sim h^{1/\delta} \\
G(r) &\sim 1/r^{d-2+\eta} \quad \text{for } \Delta T = 0 \\
\xi &\sim |\Delta T|^{-\nu}
\end{aligned}
$$

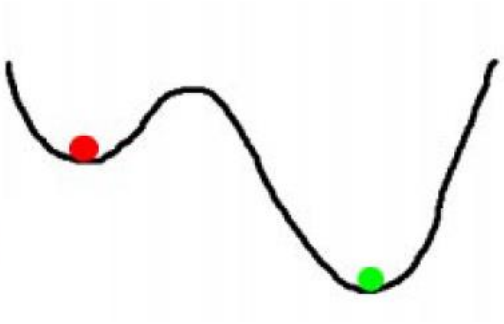
	$2D$ (exact)	$3D$ (num.)	Mean Field
α	0 (log)	0.119 ± 0.006	0 (discont.)
β	$1/8$	0.326 ± 0.004	$1/2$
γ	$7/4$	1.239 ± 0.003	1
δ	15	4.80 ± 0.05	3
η	$1/4$	0.024 ± 0.007	0
ν	1	0.627 ± 0.002	$1/2$

$$
\begin{aligned}
2\beta + \gamma &= 2 - \alpha, && \text{(Rushbrooke's law)} \\
2\beta\delta - \gamma &= 2 - \alpha, && \text{(Griffiths' law)} \\
\gamma &= \nu(2 - \eta), && \text{(Fisher's law)} \\
\nu d &= 2 - \alpha, && \text{(Josephon's law)}
\end{aligned}
$$

Dynamical exponent (non universal):

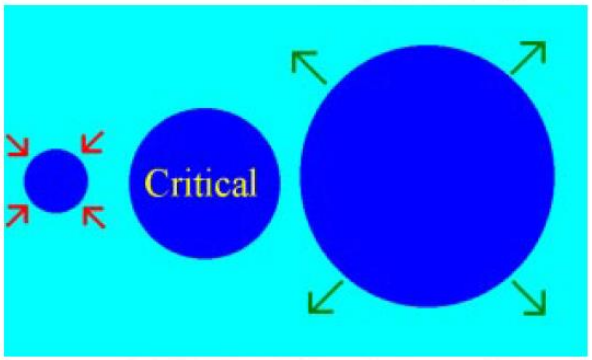
$$\tau \sim \xi^z \sim |\Delta T|^{-z\nu}$$

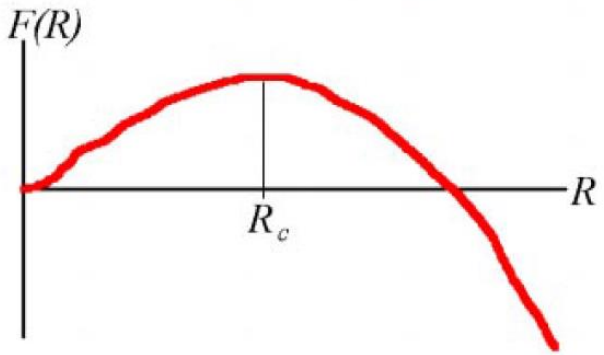
Metastability in Ising model …. and at home



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

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





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

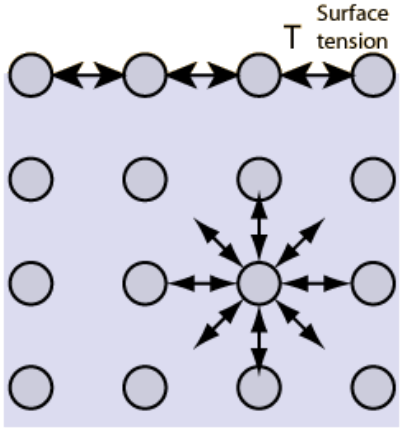
$m_s(T)$: Spontaneous magnetization.

$F(R)$ is maximum for the *critical radius* $R_c \approx \frac{(d-1)\sigma_0(T)}{2m_s(T)|H|}$

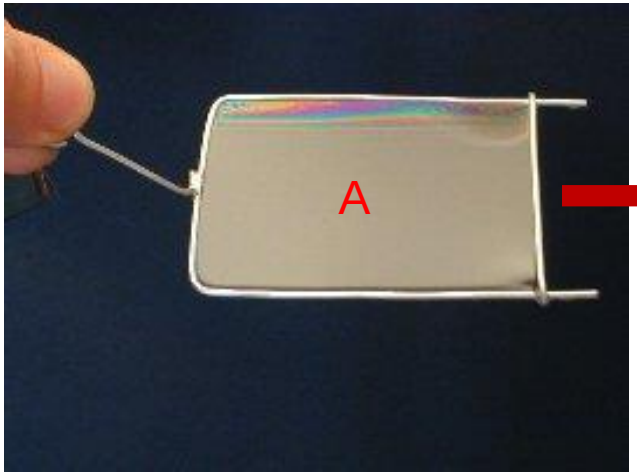
Surface tension

Molecules on the surface are less bounded than molecules in the bulk. There is therefore an energy associated with a free surface.

More rigorously: there is a free energy associated with an interface.
This energy gives rise to the surface tension σ

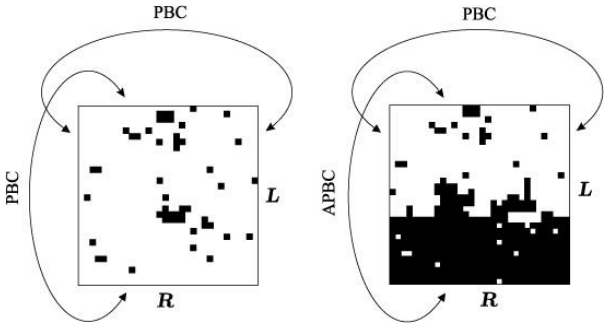


Surface tension



$$\sigma dA = Fdx$$

The energy per unit area is σ
It can often be thought of as a force



Surface tension in Ising model measures the excess free energy due to the interface

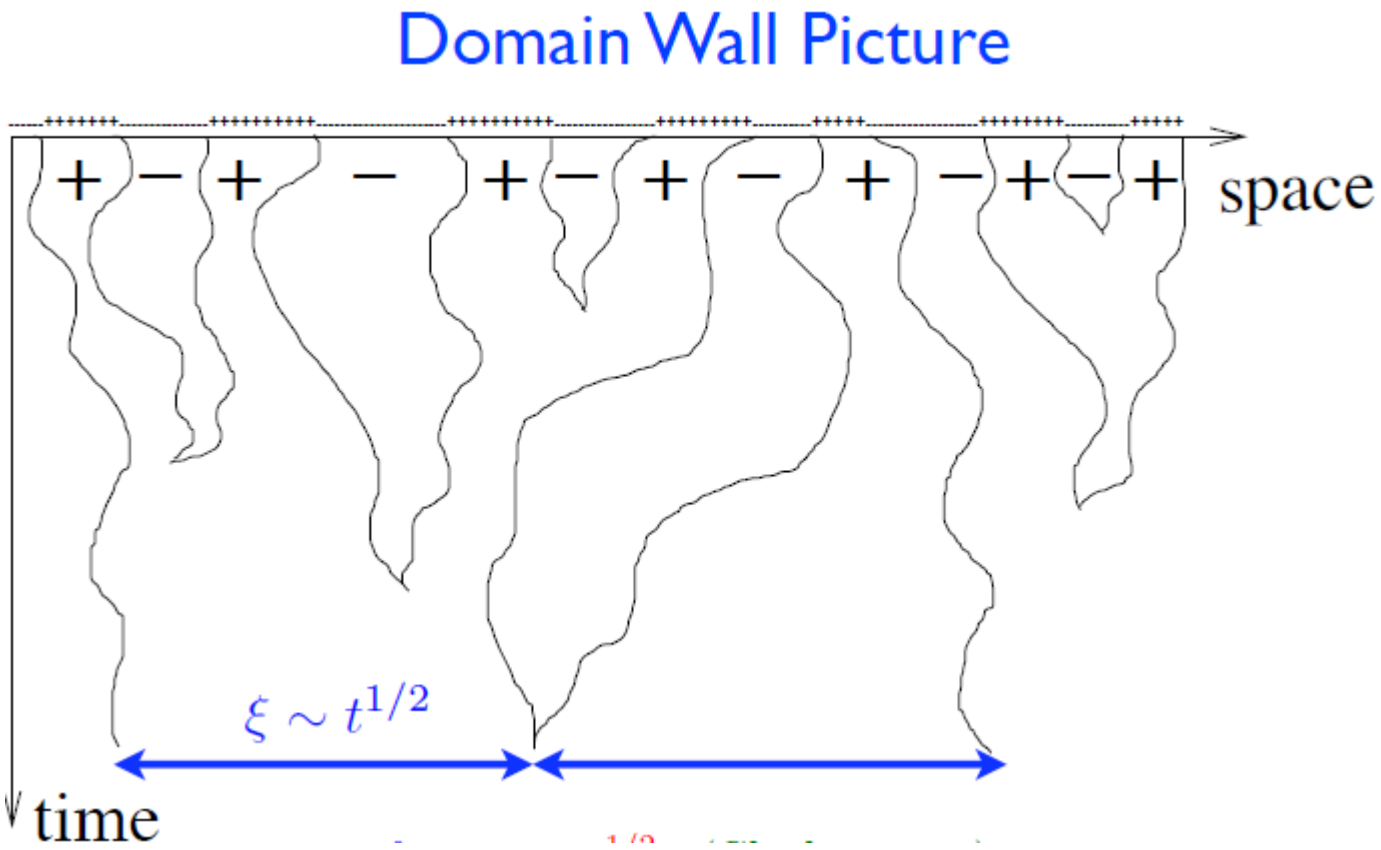
Droplet lifetime (h=0)

Laplace Law ($\Delta p = 2\sigma/R$) & Fick Law

$$\frac{dr}{dt} \sim -\frac{1}{r}$$ (Lifshitz law)

$$t \sim r^2 \ (r \sim t^{\frac{1}{2}})$$

Dynamics: one-dimensional T=0 Ising model



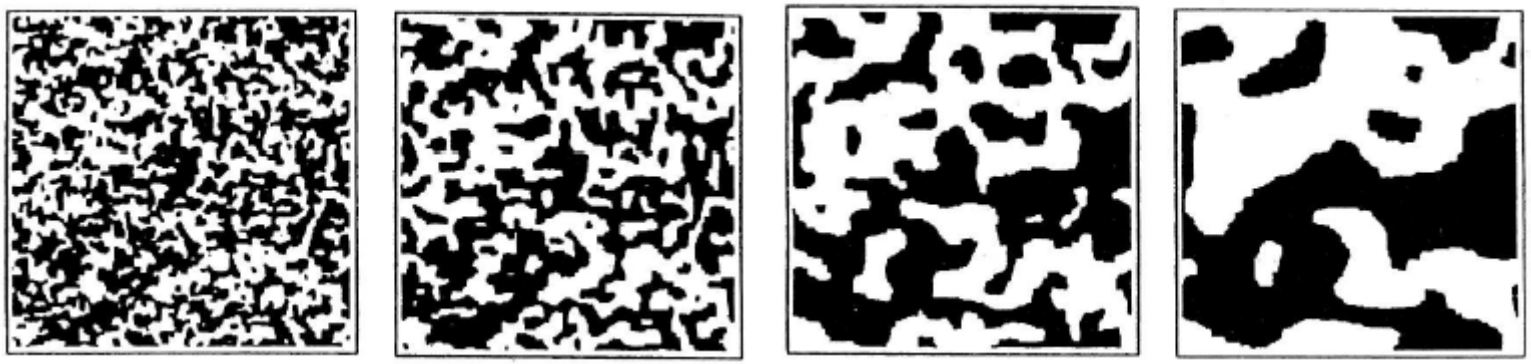
Remark: $l \sim \sqrt{t}$ holds also for d>1 models

Coarsening and aging

Systems cooled from a disordered phase into an ordered phase do not order instantaneously. The lengthscale of ordered regions grows as the different broken symmetry phases compete to select the equilibrium state.

Consider, in a Ferromagnetic Ising model, a temperature "quench" from initial temperature $T > T_c$ to final temperature $T_f < T_c$. There are two equilibrium phases at T_f, with magnetizations $\pm M_0$.

In the thermodynamic limit, final equilibrium is never achieved, because ordered regions have finite sizes at all finite times.



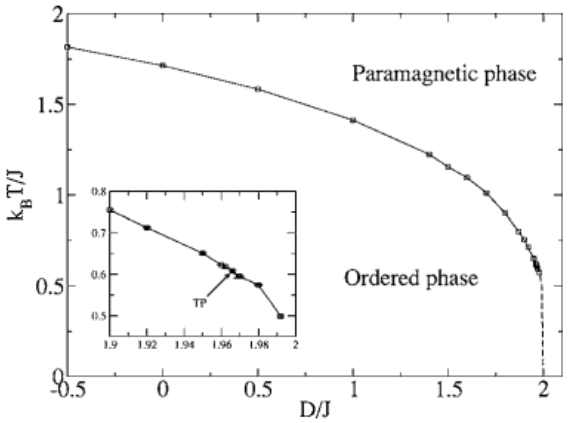
conserved vs. non-conserved dynamics

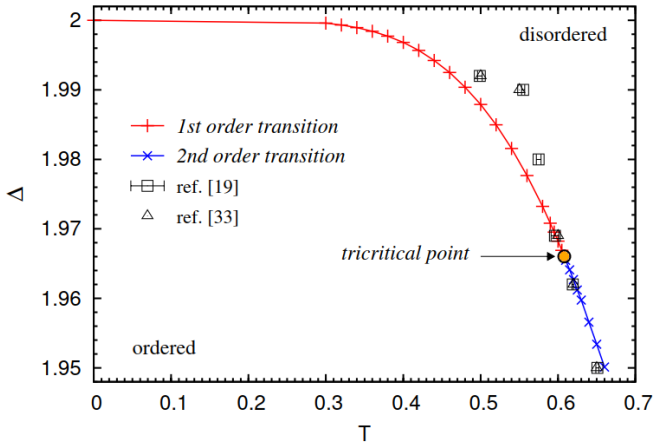
Ising model with S=1 (Blume-Capel model)

$$\mathcal{H} = -J \sum_{\langle i,j \rangle} s_i s_j + \Delta \sum_i s_i^2$$ where $s_i = -1, 0,$ or 1

- Derive the mean-field approximation for the present model
- Implement Metropolis algorithm for the present model
- Sketch its phase diagram (Δ, T)

The phase diagram of the Blume-Capel model contains a tricritical point





Recent simulations: https://arxiv.org/abs/1504.02565

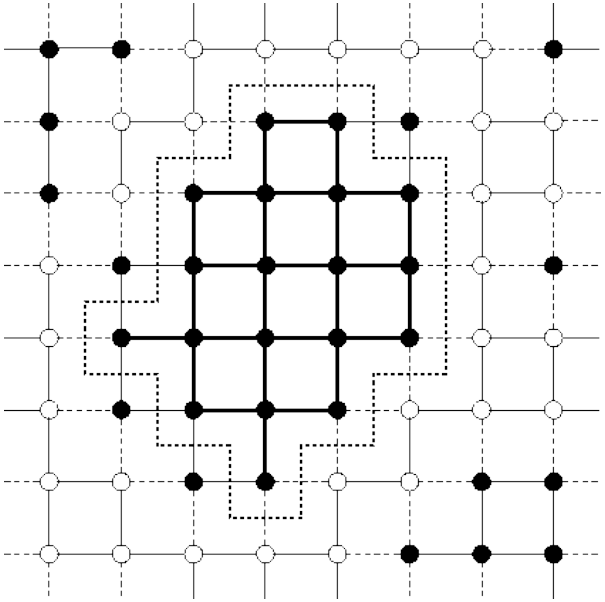
Optimization:

- Store exp(-E/T) in an array
- Cluster algorithms (for vicinity of critical points)
- Continuous time algorithm (select spins nonuniformly, but the flip is always accepted)
- histogram, multispin coding, Wang-Landau, etc…

Wulff single-cluster algorithm

[U. Wolff, PRL 62 (1989) 361]

1. Choose random site i.
2. Study neighbouring sites j. If $s_j = s_i$, join site j to cluster with probability $p = 1 - \exp(-2\beta)$.
3. Repeat step 2 for site j, if it was joined to the cluster. Keep on doing this as long as the cluster grows.
4. When the cluster is finished, invert the spins which belong to it.



Generalization.

Spins: XY,Heisenberg,Potts...

Lattices: Square, Triangle, Cubic, Honeycomb, Cayley, Kagome...

Interactions: Magnetic Field, Antiferro., Next Nearest Neighbor...

… and some more

Boundary conditions, surface effects, interfacial effects (wetting)

Exchange dynamics: exchanges pair of spins (conserves magnetiztion!)

Hard core systems, Lennard-Jones $U(r) = a(r^{-12} + br^{-6}))$

Glasses, biomolecules, …

Some versions of Ising model have local (gauge-like) symmetries.

> F.J. Wegner, Duality in generalized Ising models and phase transitions without local order parameter, J. Math. Phys. 12 (1971) 2259

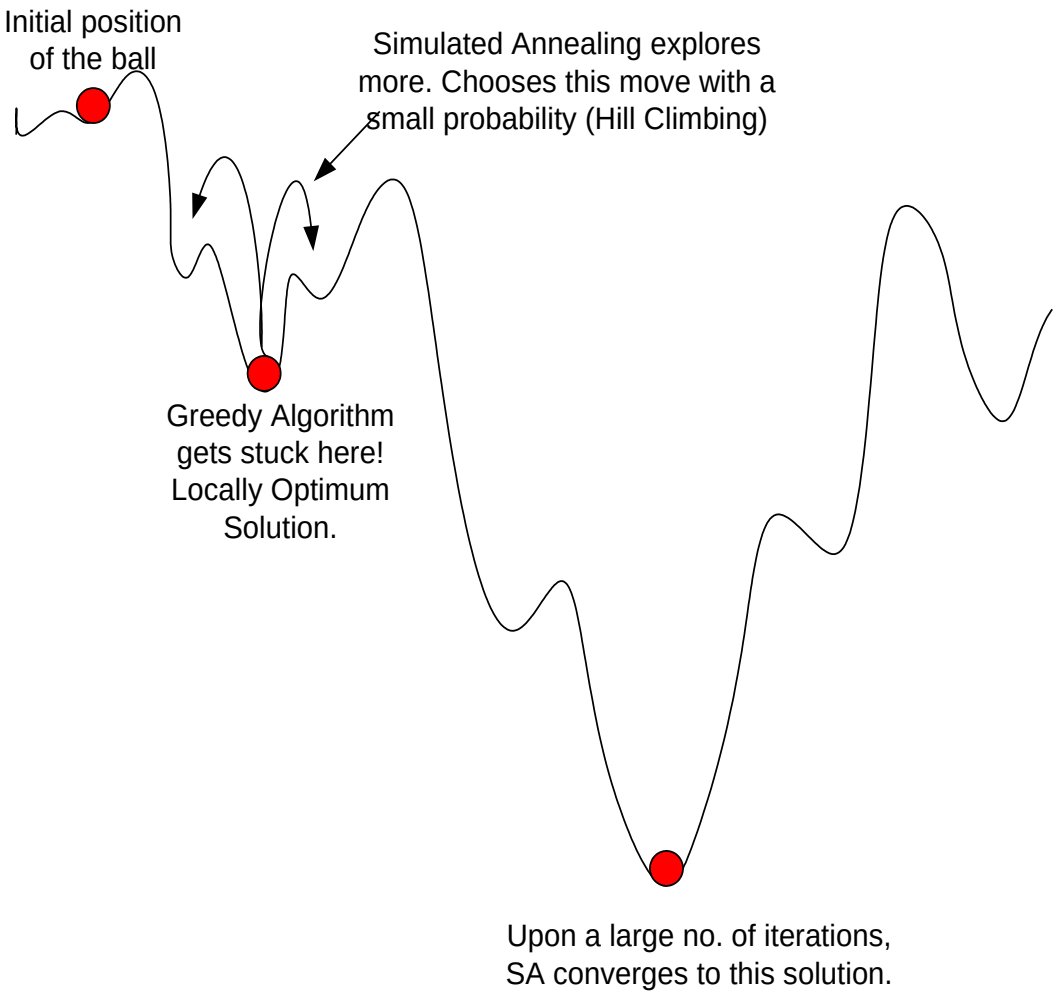
Simulated Annealing

- **Motivated by the physical annealing process**
- **Material is heated and slowly cooled into a uniform structure**
- **Simulated annealing mimics this process**
- **The first SA algorithm was developed in 1953 (Metropolis)**

Simulated Annealing

- **SA allows up-hill steps**
- **In SA a move is selected at random and then one decides whether to accept it**
- **In SA better moves are always accepted. Worse moves are accepted with some probability (that decreases during the simulations)**

SA as a movement on an energy landscape



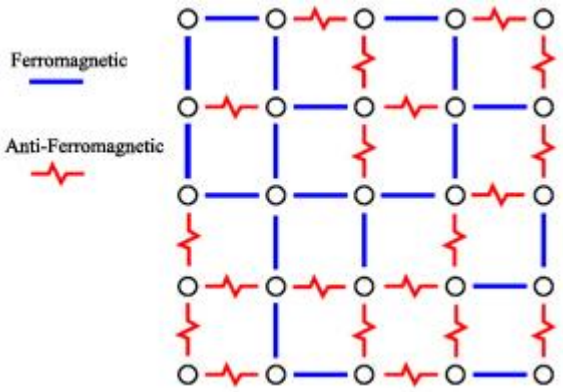
Simulated Annealing

- **Kirkpatrick (1982) applied SA to optimisation problems**

  - Kirkpatrick, S , Gelatt, C.D., Vecchi, M.P. 1983. *Optimization by Simulated Annealing*. Science, vol 220, No. 4598, pp 671-680

Spin glasses

$$H = -\sum_{<ij>} J_{i,j}\sigma_i\sigma_j$$



Find a ground state of spin glass using simulated annealing

Find a ground state using genetic algorithm

lattice type	D	μ_0	e_0 from
honeycomb	2	0.09	W. Lebrecht, E.E. Vogel *(1994)*
square	2	0.1495	I.A. Campbell, A.K. Hartmann, H.G. Katzgraber *(2004)*
triangular	2	0.22	W. Lebrecht, E.E. Vogel *(1994)*
simple cubic	3	0.202	*various authors*
hypercubic	4	0.24	S. Böttcher, A. G. Percus *(2001)*
hypercubic	5	0.26	S. Böttcher, *private communication*

(S. Kobe, J. Krawczyk in: *Computational Complexity and Statistical Physics, in press*)

- Misfit parameter → a useful rescaling of the ground-state energy per spin
- Definition: $\mu_0 = \frac{1}{2}\left(1 - e_0/e_0^{id}\right)$
- with e_0^{id} → reference energy of a related non-frustrated system: