Monte Carlo Simulations in Statistical Physics

Classical interacting many-particle systems; examples

- atoms and molecules in simple liquids, gases, solids
- macromolecular systems; polymers, liquid crystals
- spin models of magnetism

Quantum fluctuations can often be neglected (not always)

Problem: Evaluate thermal expectation values

N particles with positions and momenta $\vec{x}_i,\ \vec{p}_i$

$$\langle A \rangle = \frac{1}{Z} \int \prod_{i=1}^{N} dx_i^d \int \prod_{i=1}^{N} dp_i^d A(\{x_i, p_i\}) \mathrm{e}^{-H(\{x_i,p_i\})/k_B T}$$

Partition function (state sum)

$$Z = \int \prod_{i=1}^{N} dx_i^d \int \prod_{i=1}^{N} dp_i^d \mathrm{e}^{-H(\{x_i,p_i\})/k_B T}$$

Hamiltonian (energy function) for identical particles in potential U and with pair-interaction V

$$H(\{\vec{x}_i, \vec{p}_i\}) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + \sum_{i=1}^{N} U(\vec{x}_i) + \sum_{i \neq j} V(\vec{x}_i, \vec{x}_j)$$

If the observable A is velocity-independent (real-space correlation functions, response of local density to external perturbations, etc.), the momentum integrals cancel

$$\langle A \rangle = \frac{1}{Z} \int \prod_{i=1}^{N} dx_i^d A(\{x_i\}) \mathrm{e}^{-E(\{x_i\})/k_B T}$$

$$Z = \int \prod_{i=1}^{N} dx_i^d \mathrm{e}^{-E(\{x_i\})/k_B T}$$

Only the potential energy matters

$$E(\{x_i\}) = \sum_{i=1}^{N} U(\vec{x}_i) + \sum_{i \neq j} V(\vec{x}_i, \vec{x}_j)$$

For the kinetic energy the position integrals cancel

$$\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{1}{Z_p} \int dp_i^d \frac{p_i^2}{2m} \mathrm{e}^{-p_i^2/2mk_BT}$$

$$Z_p = \int dp_i^d \mathrm{e}^{-p_i^2/2mk_BT}$$

This gives the equipartition theorem $\left\langle \frac{p_i^2}{2m} \right\rangle = \frac{d}{2} k_B T$

Most of statistical physics concerns velocity-independent quantities; the mathematical problem of interest is

$$\langle A \rangle = \frac{1}{Z} \int \prod_{i=1}^{N} dx_i^d A(\{x_i\}) \mathrm{e}^{-E(\{x_i\})/k_BT}$$

$$Z = \int \prod_{i=1}^{N} dx_i^d \mathrm{e}^{-E(\{x_i\})/k_BT}$$

With N approaching infinity (thermodynamic limit)

Few exact solutions; numerical simulations for finite N important

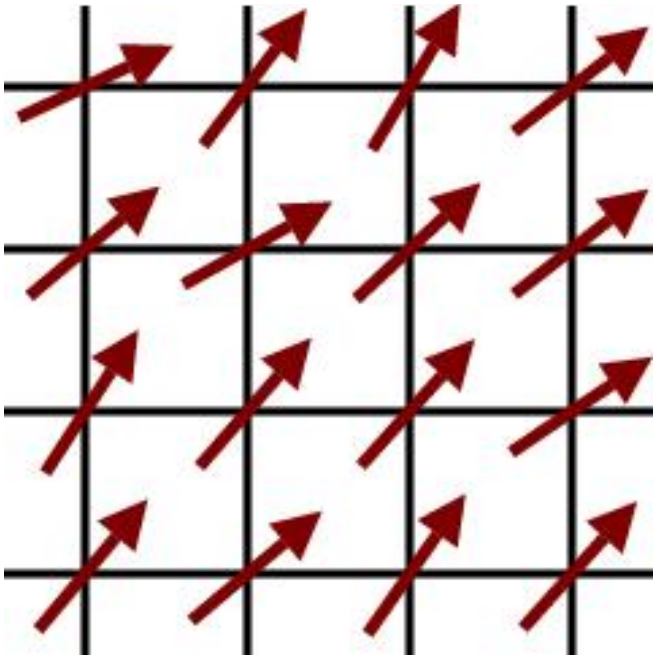
Lattice and spin models

Degrees of fredom "live" on vertices of a lattice

- Continuous or discrete variables on the vertices

Spin models, describing magnetism of solids with spinful atoms

- large spin S behaves as classical angular momentum
- quantum fluctuations important for small S (1/2,1,3/2)



Interactions: often of the Heisenberg form

$$E = \sum_{i,j} J_{ij} \vec{S}_i \cdot \vec{S}_j$$

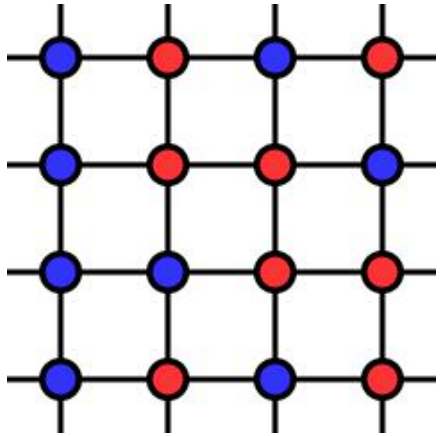
Ising models

Two states on each lattice site $\text{spin} \uparrow, \downarrow$

Can arise for quantum mechanical S=1/2: $S_i^z = \pm 1/2$

Strong anisotropies; z-interactions can dominate

$$E = \sum_{i,j} J_{ij} S_i^z S_j^z$$



This is the Ising model

- important in the theory of magnetism
- also effective model for other stat mech problems ("lattice gases", binary alloys, atom adsorption on surfaces,...)

With only nearest-neighbor interactions (J), the Ising model can be solved analytically in 1D and 2D

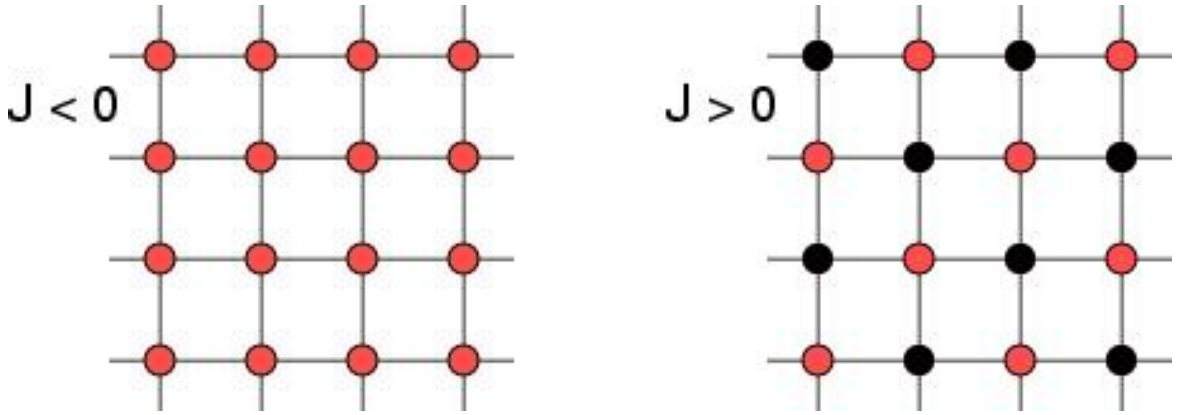
- Numerical simulations important in most other cases

Two-dimensional Ising model

$$E = J \sum_{\langle i,j \rangle} \sigma_i \sigma_j, \quad \sigma_i = \pm 1$$

$\langle i, j \rangle$ denotes nearest neighbors

Ferromagnetic or antiferromagnetic ground state (T=0)



Related by transformation: $\sigma_i \longrightarrow -\sigma_i$ on one sublattice

Thermal expectation value of some quantity A

$$\langle A \rangle = \frac{1}{Z} \sum_S A(S) \mathrm{e}^{-E(S)/T}, \quad Z = \sum_S \mathrm{e}^{-E(S)/T}$$

Phase transition

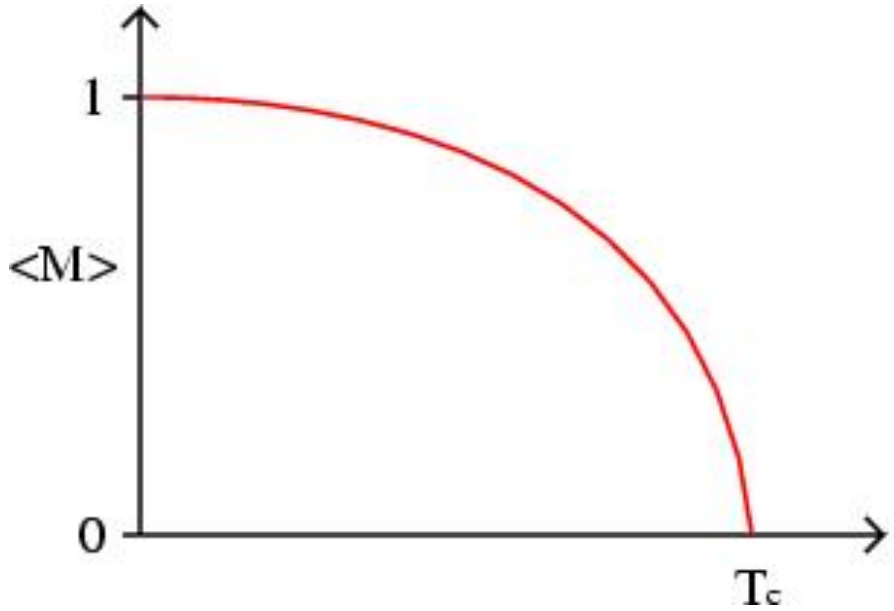
Spontaneous ordering (symmetry breaking) at critical temperature

magnetization (ferromagnet)

$$T_c/J = 2/\ln(1+\sqrt{2})$$

$$T_c/J \approx 2.269$$

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



Broken symmetry
only in infinite system

<M>=0 for finite N

<M^2> or <|M|> can be used

sublattice (staggered) magnetization (antiferromagnet)

$$M = \frac{1}{N}\sum_{i=1}^{N}(-1)^{x_i+y_i}\sigma_i$$

Monte Carlo simulations of the 2D Ising model

Stochastic sampling of spin configurations to estimate

$$\langle A \rangle = \frac{1}{Z} \sum_S A(S) \mathrm{e}^{-E(S)/T}, \quad Z = \sum_S \mathrm{e}^{-E(S)/T}$$

Spin configurations $S = (\sigma_1, \sigma_2, \ldots, \sigma_N)$

2^N configurations; can sample very small fraction for large N

Trivial Monte Carlo sampling fails at low T, because the sum is then dominated by configurations with large ordered domains, which are very unlikely to be generated in random sampling

Extreme case: T=0. Only two configurations contribute, but the probability to generate them is $1/2^{N-1}$

Solution: **Importance sampling:**

- Generate configurations according to Boltzmann distribution

Importance sampling

First, rewrite expectation value as

$$\langle A \rangle = \sum_S P(S)A(S), \quad P(S) = \frac{1}{Z} \mathrm{e}^{-E(S)/T} \quad W(S) = \mathrm{e}^{-E(S)/T}$$

P(S) can be interpreted as the probability of configuration S
- W(S) is called the weight of the configuration

Uniform sampling of N configurations

$$\langle A \rangle \approx \frac{\sum_{i=1}^{N} W(S_i)A(S_i)}{\sum_{i=1}^{N} W(S_i)}$$

Importance sampling: The probability to pick S is P(S)

$$\langle A \rangle \approx \frac{1}{N} \sum_{i=1}^{N} A(S_i)$$

This sampling selects exactly the important configurations, and hence the statistical errors will be much smaller at low T.

But how do we accomplish importance sampling in practice?

Imagine **ensemble** of huge number of states in equilibrium

Number of states A is $N_0(A)$, proportional to P(A)

We now make some random change in each state (e.g., flip spins)

Possible transitions: $A \to B, C, \ldots$

Number of states A after the "update"

$$N_1(A) = N_0(A) + \sum_{B \neq A} N_0(B)P(B \to A) - N_0(A)P(A \to B)$$

This is the **master equation** for the stochastic process

If we want the distribution to remain P(A) after the update

$$\sum_{B \neq A} N_0(B)P(B \to A) - N_0(A)P(A \to B) = 0$$

$$\sum_{B \neq A} P(B)P(B \to A) - P(A)P(A \to B) = 0$$

Many possible solutions; an obvious solution, called the **detailed-balance** solution (condition): For every A, B

$$P(B)P(B \to A) = P(A)P(A \to B)$$

Time evolution of a single configuration; **Markov process**

Time average of a Markov process same as ensemble average

If we make random updates on a single configuration, and satisfy detailed balance, $P(B)P(B \to A) = P(A)P(A \to B)$, and if the updates are such **that any configuration can be reached in a series of updates (ergodicity).**

Then, the **time distribution of configurations A will approach the distribution P(A) independently of the initial configuration**

Alternative form of the detailed-balance condition

With $P(A) = \exp[-E(A)/T]/Z = W(A)/Z$

$$\frac{P(B \to A)}{P(A \to B)} = \frac{W(A)}{W(B)}$$

We have to construct transition probabilities satisfying this