Intro to Stat Mech

Ex: ferromagnet

Ising Model: 1D chain

$\uparrow \downarrow \uparrow \uparrow \downarrow \uparrow \uparrow \; = \; + - + + - + +$

$E_{i,j} = -\varepsilon s_i s_j$ (nearest neighbors) $\varepsilon > 0$

$$H = \sum_{(i,j)} E_{ij} = -\varepsilon \sum_{(i,j)} s_i s_j = \boxed{-\varepsilon \sum_{i=1}^{N} s_i s_{i+1} \equiv E}$$

$\uparrow \uparrow \downarrow \uparrow$

$\uparrow \uparrow \uparrow \downarrow$

$$\boxed{\underline{M} = \sum_i \underline{s}_i}$$

$$s_i = \begin{cases} +1 & \text{up}, + \\ -1 & \text{down}, - \end{cases}$$

microstate: $\{s_i\}_{1 \le i \le N}$

macrostate: macro observable E, M

$$\langle M(\{s_i\}) \rangle_{\{s_i\}} = M$$

micro			macro
+	+	+	3
+	+	−	1
+	−	+	1
−	+	+	1

Temperature : tendency of heat flow

1st law : $\Delta U = \text{heat} + \text{work} = Q + W$

$\Delta U = T \Delta S - p \Delta V + \mu \Delta N$

entropy (S); chem pot. (μ)

$dU = T dS - p dV + \mu dN$

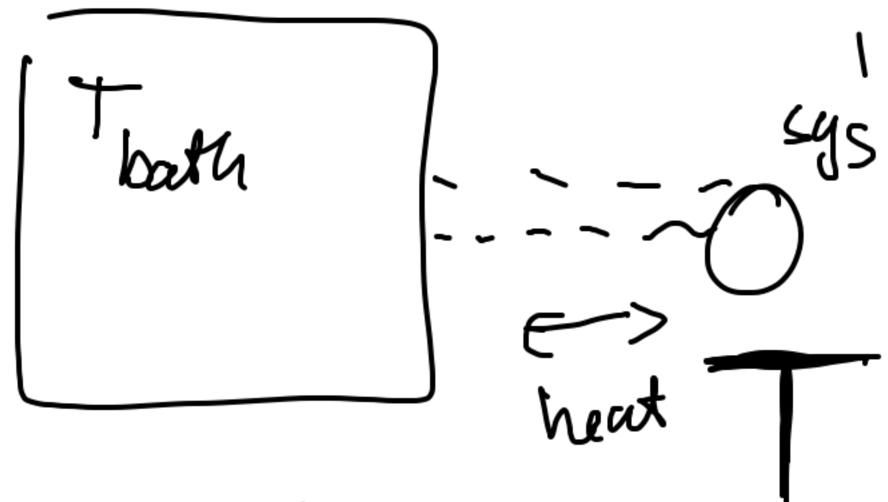
Boltzmann's constant

$S = k \ln \Omega$

Ω: multiplicity of states

$k = 1.38 \times 10^{-23} \frac{J}{K}$

Heat bath



EQUILIBRIUM

$T_{sys}^{init} \longrightarrow T_{sys} = T_{bath}$

$\boxed{\text{Equilibrium}}$ $N = \text{const}$ $V = \text{const}$ "canonical ensemble"

$T = \text{const}$ (NVT)

nothing (big) changes

$$\frac{d\Theta}{dt} = 0$$

Boltzmann distribution

In NVT equilibrium state with energy E have prob

$$P(E) \propto \exp(-E/kT) \qquad \beta = \frac{1}{kT}$$

$$\boxed{\begin{aligned} P(E_n) &= \frac{1}{Z} e^{-\beta E_n} \\ Z &= \sum_n e^{-\beta E_n} \end{aligned}}$$

$\leftarrow$ BOLTZMANN distrib

$\leftarrow$ partition function

States chain N: $\Omega = 2^N$

$N = 10^{24} \quad 2^{10^{24}} \approx 10^{300}$

Avg Energy:

$$\langle E \rangle = \sum_n E_n P(E_n) = \sum_n E_n \frac{1}{Z} e^{-\beta E_n}$$

$$= Z^{-1} \sum_n \left(-\frac{\partial}{\partial \beta} e^{-\beta E_n}\right) = -Z^{-1} \frac{\partial}{\partial \beta} \underbrace{\sum_n e^{-\beta E_n}}_{Z} = -\frac{1}{Z} \frac{\partial Z}{\partial \beta} = -\frac{\partial \ln Z}{\partial \beta}$$

$F = -\beta^{-1} \ln Z$ (free energy)

$C = \frac{\partial \langle E \rangle}{\partial T} = \frac{1}{kT^2}\left(\langle E^2 \rangle - \langle E \rangle^2\right)$ (heat capacity)

$$p_1 = \frac{1}{Z} e^{-\beta E_1}$$

$$p_2 = \frac{1}{Z} e^{-\beta E_2}$$

$$\begin{array}{ccc} 1 & \longleftrightarrow & 2 \\ E_1 & & E_2 \end{array}$$

$$\frac{p_2}{p_1} = \frac{Z^{-1} e^{-\beta E_2}}{Z^{-1} e^{-\beta E_1}} = e^{-\beta(E_2 - E_1)} = \boxed{e^{-\beta \Delta E_{21}} = \frac{p_2}{p_1}}$$

Relative probabilities between states are governed by the Boltzmann factor of the energy difference between stares.

This applies to any states — micro or macro — as long as the system is in equilibrium.

1D Ising model

$$H = -\varepsilon \sum_{\langle i,j \rangle} s_i s_j$$

$$p(\{s_i\}) \propto e^{-\beta H(\{s_i\})}$$

$\langle M \rangle$

$$\langle E \rangle = \sum_{\text{states}} E(\{s_i\})\, e^{-\beta H(\{s_i\})}$$

Sampling process in important regions of state space

Metropolis algorithm

E' : trial

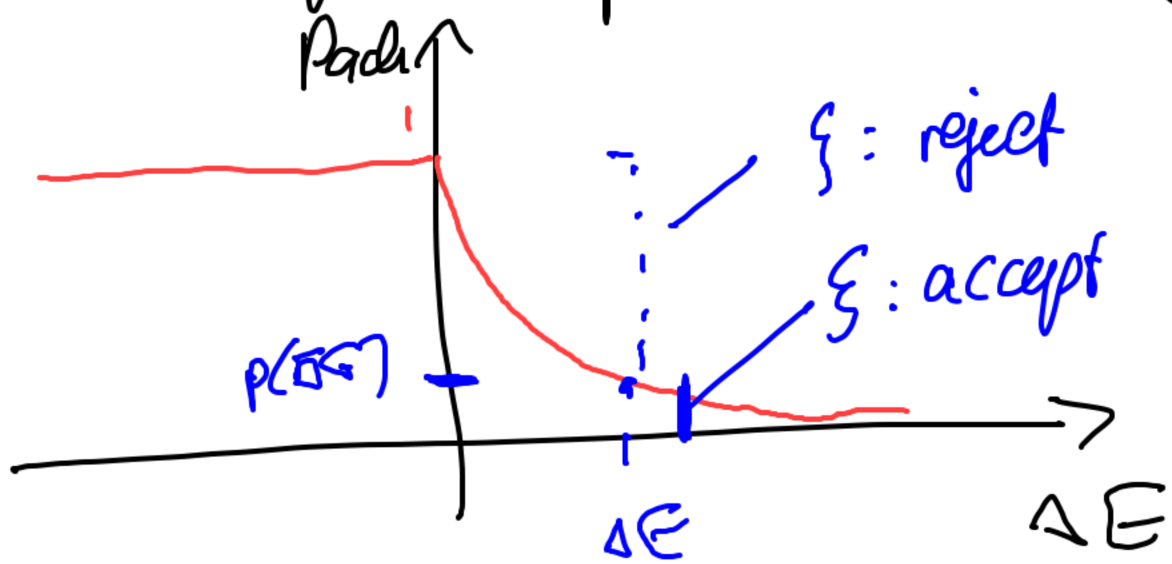
E : current energy

thermal fluct $\sim kT$

$$e^{-\beta E} = e^{-\frac{E}{kT}}$$

1) pick s_i randomly
2) flip spin (trial)
   calc. $\Delta E = E' - E$
3) acceptance
   $\Delta E < 0$: accept
   $\Delta E \geq 0$: accept with prob $e^{-\beta \Delta E}$
4) goto 1

accept step: $p_{acc} = \min(1, e^{-\beta \Delta E})$



"rejection sampling"

$\xi \sim \mathcal{U}_{[0,1]}$

Keep accepted <u>and</u> rejected steps (= prev.)

$$\Delta E = H(\text{trial}) - H(\text{current}) = E' - E$$

ΔE

$$\ldots \uparrow \Uparrow \downarrow \ldots$$
$$s_{k-1} \; s_k \; s_{k+1}$$

$$E = -\varepsilon(s_{k-1}s_k + s_k s_{k+1}) = -\varepsilon s_k(s_{k-1} + s_{k+1})$$

$$E' = +\varepsilon s_k(s_{k-1} + s_{k+1})$$

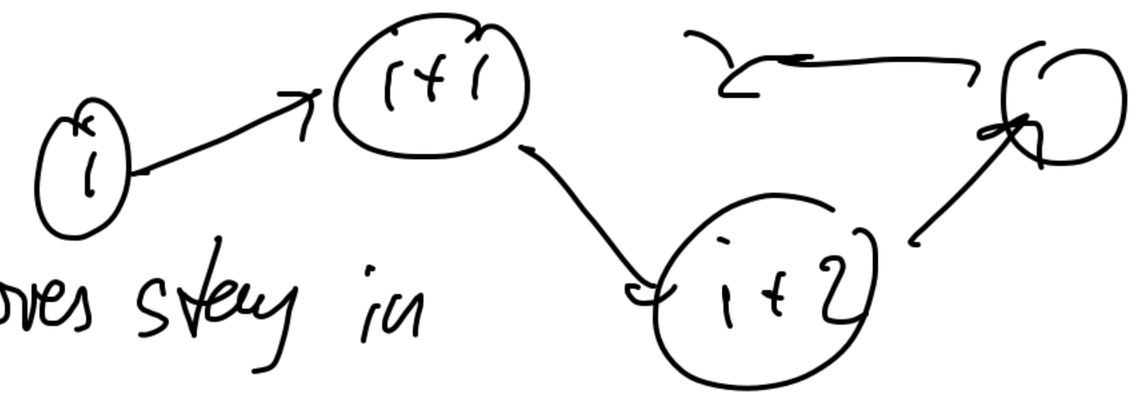
$$s_k \to s_k' = -s_k \qquad \boxed{\Delta E = 2\varepsilon s_k(s_{k-1} + s_{k+1})}$$

Periodic boundary cond.

$$s_0 \equiv s_N$$

Why does Metropolis work:

(Markov Chain MC)



1) sequence of moves: moves stay in state space

2) Markov cond: prob to go from $i \to k$ only depends on i

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flip spin $1 \to 2$

assume: $E_1 < E_2$: $\Delta E > 0$

accept $p \propto e^{-\beta \Delta E}$

rate of state changes $k_{12} = e^{-\beta(E_2 - E_1)}$

in the opposite dir. $2 \to 1$ $\Delta E < 0$

accept : 1 $k_{21} = 1$

Equilibrium: ~~DE~~TAILED BALANCE

number of transitions $1 \to 2$ = number of transitions $2 \to 1$

flux 1->2 flux 2->2

$$\phi_{12} = \phi_{21}$$

probability flux = probability to be in initial state x rate to go from initial to final state

$$\boxed{p_1 k_{12} = p_2 k_{21}}$$

$$p_1 e^{-\beta \Delta E} = p_2 \cdot 1$$

$$\boxed{\frac{p_2}{p_1} = e^{-\beta \Delta E} = e^{-\beta(E_2 - E_1)}}$$

Metropolis: system states are Boltzmann distribute

The probability ratio will be the Boltzmann factor for ANY states 1 and 2, so the Metropolis procedure will correctly sample from the Boltzmann distribution for all moves that follow the Metropolis criterion (and are "ergodic", i.e., any state can eventually be reached).