detailed balance

$p_{\text{original state}} \cdot P(\overset{\text{generate}}{\text{forward}})\ P(\text{accept forward})$ — suppose $= 1$

$= p_{\text{new state}}\ P(\overset{\text{generate}}{\text{backward}})\ P(\text{accept backward})$

(so not $\exp(-\beta \Delta U)$ can't be, becaus $P(\text{forward}) \neq P(\text{back}$

$\exp(-\beta U)$ $\qquad \exp(-\beta(U - 2J\Delta))$

$$P(\text{forward}) / P(\text{backward}) = \exp(+\beta 2J\Delta) = (1-p)^{-\Delta}$$

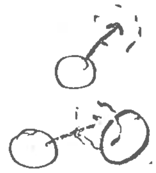
$$\Rightarrow \exp(-\beta 2J) = 1-p$$

$\Rightarrow$ allways accept and you speed up convergence!

In general not always possible

Early rejection: figure out early on that a move is doomed and never calculate all of it.

- hard-core interactions
- strongly repulsive component. if $\Delta U >$ something



— doomed, no need to check the rest

Ensembles in MC : same as thermostats in MD; get right dist

- So far, done NVT

Microcanonical MC

- generate trial move as usual
- extra variable : E_D
- modify acceptance.

  if $\Delta U < 0$; accept, $\quad E_D \mathrel{+}= \Delta U$

  if $\Delta U > 0$, $E_D > \Delta U$: accept $\quad E_D \mathrel{-}= \Delta U$

  $\qquad\qquad$, $E_D < \Delta U$: reject

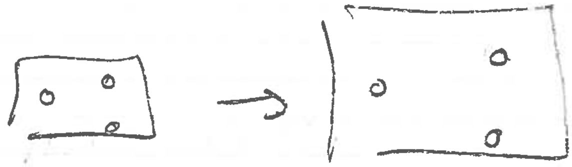
acceptance not random, but generation of trial move is wiggle around conserved energy. $U + E_D$ conserved. in principle should include kinetic term as well

not used much.

MC in NPT ensemble

- common experimental situation
- construction similar to barostat

- rescale the system
  V as variable



V_{old} V_{new}

distribution

$$\int dr \, \exp[-\beta(U+PV)] \rightarrow \int ds \, \underbrace{\overbrace{V^N}^{\text{jacobian}} \exp[-\beta(U+PV)]}$$

ds: scaled coordinate

what we need to construct.

step (1) trial move,
either (a) normal NVT move
or (b) change in volume:

$$r \rightarrow r\left(\frac{V_{new}}{V_{old}}\right)^{1/3}$$

step (2) accept (a) according to Metropolis
or (b) according to

$$P = \min\Big(1, \underbrace{\exp[-\beta(\Delta U + P\Delta V)]\left[\frac{V_{new}}{V_{old}}\right]^N}_{\tilde{p}}\Big)$$

detailed balance

$$P(\rightarrow) \cdot V_{old}^N \exp[-\beta(U_{old} + PV)] = P(\leftarrow)\, V_{new}^N \exp[-\beta(U_{new} + PV)]$$

$$\min(1, \tilde{p}) \qquad = \qquad \min\left(1, \frac{1}{\tilde{p}}\right) \quad \tilde{p}$$

$\Rightarrow$ true!

ΔU due to change of volume is demanding to calculate
trick for powerlaw potentials (such as LJ)

$$V_{LJ} = 4\epsilon \left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6} \right]$$

save seperately. V_{12}, V_6

$$r \rightarrow \left(\frac{V_{new}}{V_{old}}\right)^{1/3} r \quad , \text{ so}$$

$$V_{12} \rightarrow V_{12} \left(\frac{V_{new}}{V_{old}}\right)^{-4}$$

$$V_6 \rightarrow V_6 \left(\frac{V_{new}}{V_{old}}\right)^{-2}$$

end lecture 11

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grand canonical μVT | i.e small system $\subset$ bigger system

- normal NVT or
- insert / remove particles

careful with normalisation again $\quad \propto \frac{V^N}{\Lambda^{3N} N!} \int dr_1 \dots dr_N \exp[-\beta(U - \mu N)]$

Λ: de Broglie wavelength

insert at random position / remove random particle } with equal prob. $\Rightarrow$ symmetry

$$P(N \to N+1) = \min\left(1, \frac{V}{\Lambda^3 (N+1)} \exp[-\beta(\mu - \Delta U)]\right)$$

$$P(N \to N-1) = \min\left(1, \frac{\Lambda^3 N}{V} \exp[-\beta(\mu + \Delta U)]\right)$$

one = 1 other not

check detailed balance

$$P(N \to N+1) \frac{V^N}{\Lambda^{3N} N!} \exp[-\beta(U_N - \mu N)]$$

$$= P(N+1 \to N) \frac{V^{N+1}}{\Lambda^{3(N+1)} (N+1)!} \exp[-\beta(U_{N+1} - \mu(N+1))]$$

$\Rightarrow$ everything matches nicely.

problem: at high density $\Rightarrow \Delta U$ very big $\Rightarrow$ low acceptance rate

solution: position dependent insertion rate (trick with symmetry)

$\leftarrow$ high prob of overlap.

can also use for multi component mixture $\mu_1 \mu_2$ (chemical reactions)

(take care to insert / remove species with same prob)

- select species first

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combine for μPT