bond stretching, bending, torsion etc

FK 7029
(33)

easiest if just full 3d eq of motion per particle. (no rigid constraints)

- treat all atoms individually
- take care to use small displacement for tightly bound atoms
  $\Rightarrow$ not so efficient.

rigid constraints
- do explicitly
- for large molecules become difficult, MD easier.

[illegible]

(unlike MD)

Important point: Trial moves need not be physical

as long as the reverse has same prob $\Rightarrow$ detailed balance

Cluster moves.

Remember Ising model at low T, $\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow$ $\downarrow\downarrow\downarrow\downarrow\downarrow\downarrow$

- in principle conf all ↑ an all ↓ are connected, by very unlikely sequence of moves due to high energy barrier

flipping 1 spin at a time will not make this transition,

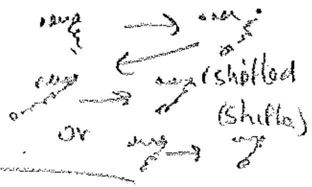
(common problem in MC & MD)

MC moves can bypass U-barriers: Cluster moves.
- internal interactions in cluster unchanged
- interaction with environment changes.

$\Rightarrow$ best clusters: $\Delta E \approx 0$ $\Rightarrow$ high acceptance.

or tune acceptance probs

example: moving C.O.M of molecule



example: Ising model.

$\uparrow\!-\!\uparrow\!\times\!\downarrow\!\times\!\downarrow$
$\uparrow\!\times\!\downarrow\!\times\!\uparrow\!\times\!\downarrow$ etc. $H = -\sum_{nn} J S_i S_j$

$\uparrow$ assume positive.

$U = (N_a - N_p) J$
anti-parallel # parallel

cluster: connecting neighbours
- not if antiparallel,
- prob p if parallel

suppose we flip the subset of clusts, which will send $N_p' = N_p + \Delta$
$N_a' = N_a - \Delta$

$U' = U - 2J\Delta$

connected spins

broken spins

prob of forward move generated: $p^{n_c} (1-p)^{N_p - n_c}$

backward move

$\neq p^{n_c'} (1-p)^{N_p' - n_c'}$

violate detailed balance?

generate same set of clusters from other config

$n_c' = n_c$
must flip same cluster back

$P(\text{forward}) / P(\text{backward}) = (1-p)^{-\Delta}$

detailed balance

$p_{\text{originalstate}} \cdot P(\overset{\text{generate}}{\text{forward}})\ P(\text{accept forward})$

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

suppose =1

(so not exp-(βΔU)) can't be, becau P(forward)≠P(backw

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

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

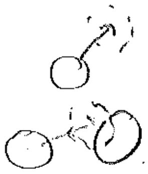
$\Rightarrow \exp(-\beta 2J) = 1-p$

$\Rightarrow$ 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 ΔU > 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, $E_D \mathrel{+}= \Delta U$

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

  , $E_D < \Delta U$: reject

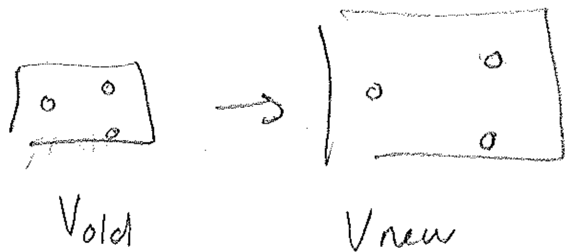
acceptance not random, but generation of trial move is wiggle around conserved energy. $U + E_D$ conserved.
in principle should include kinetic term as well
not used much.

MC in NPT ensemble

- common experimental situation
- construction similar to barostat

→ rescale the system

V as variable



distribution

$$\int dr \, \exp[-\beta(U+PV)] \cong \int \underset{\uparrow \text{ scaled coordinate}}{ds} \, \underbrace{\overset{\text{jacobian}}{V^N} \exp[-\beta(U+PV)]}_{\text{what we need to construct}}$$

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

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

step ② accept ⓐ according to Metropolis
or ⓑ 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

$$\underset{\min(1,\tilde{p})}{\underset{\downarrow}{P(\rightarrow)}} \cdot V_{old}^N \exp[-\beta(U_{old}+PV)] = \underset{\min(1,\frac{1}{\tilde{p}})}{P(\leftarrow)} \underset{\tilde{p}}{V_{new}^N \exp[-\beta(U_{new}+PV)]}$$

⇒ true!

— end lecture 10