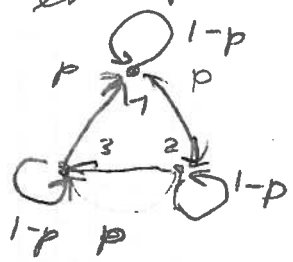
example (2)



$$p_{ij} = \begin{pmatrix} 1-p & 0 & p \\ p & 1-p & 0 \\ 0 & p & 1-p \end{pmatrix} \rightarrow a = \left(\tfrac{1}{3}, \tfrac{1}{3}, \tfrac{1}{3}\right)$$

(compare to  ⇒ no balance (3.3))

approach equilibrium?

if $p \neq 0, 1$! Then let's look at sequence $\tilde{a}(1) \dots \tilde{a}(n)$

$$\tilde{a}_1(n) = (1-p)\,\tilde{a}_1(n-1) + p\,\tilde{a}_3(n-1) \text{ etc}$$

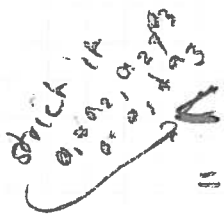
$$(\tilde{a}(n) - a)^2 = (1-p)^2 \tilde{a}_1(n-1)^2 + p^2 \tilde{a}_3(n-1)^2 \quad \text{(don't write, too much work)}$$

$$+ 2(1-p)p\,\tilde{a}_1\tilde{a}_3 + \tfrac{1}{3}^2 - \tfrac{2}{3}\left[(1-p)\tilde{a}_1 + p\tilde{a}_3\right]$$

$$+$$

$$(\tilde{a}(n) - a)^2 = \left((1-p)^2 + p^2\right)\left(\tilde{a}_1^2 + \tilde{a}_2^2 + \tilde{a}_3^2\right)$$

$$+ 2p(1-p)\left[\tilde{a}_1\tilde{a}_2 + \tilde{a}_1\tilde{a}_3 + \tilde{a}_2\tilde{a}_3\right] + \tfrac{1}{3} - \tfrac{2}{3}\left(\tilde{a}_1 + \tilde{a}_2 + \tilde{a}_3\right)$$



$$\dots + 2p(1-p)\left[\tilde{a}_1^2 + \tilde{a}_2^2 + \tilde{a}_3^2\right] + \tfrac{1}{3} - \tfrac{2}{3}\left(\tilde{a}_1 + \tilde{a}_2 + \tilde{a}_3\right)$$

$$= \tilde{a}_1^2 + \tilde{a}_2^2 + \tilde{a}_3^2 + \tfrac{1}{3} - \tfrac{2}{3}\left(\tilde{a}_1 + \tilde{a}_2 + \tilde{a}_3\right)$$

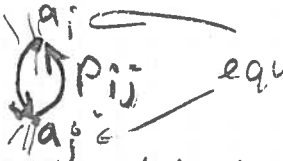
$$= \left(\tilde{a}_1 - \tfrac{1}{3}\right)^2 + \left(\tilde{a}_2 - \tfrac{1}{3}\right)^2 + \left(\tilde{a}_3 - \tfrac{1}{3}\right)^2 = \left(\tilde{a}(n-1) - a\right)^2$$

⇒ convergence!

---

detailed balance (locally in balance)

$$p_{ji}\,a_i = p_{ij}\,a_j$$



equilibrium populations

the same flow both ways (micro reversibility)

example ③ above does not have detailed balance, but just balance

example ① has detailed balance

strictly, only balance sufficient, but detailed balance more practical and not slower

---

Now we see how to enforce $\frac{1}{Z}\exp(-\beta E_i)$

We want $a_i = \exp(-\beta E(\alpha_i))$

$$p_{ji}\exp(-\beta E(\alpha_i)) = p_{ij}\exp(-\beta E(\alpha_j))$$

Metropolis algorithm

$\uparrow\uparrow\downarrow\uparrow \rightarrow \uparrow\downarrow\downarrow\uparrow$

① generate new state α_j from old one α_i (f.e flip one spin)

② accept with p_{ji} probability with

$$p_{ij} = \begin{cases} 1 & \text{if } E(\alpha_j) \leq E(\alpha_i) \\ \exp\left[-\beta(E(\alpha_j) - E(\alpha_i))\right] & \text{if } E(\alpha_j) > E(\alpha_i) \end{cases}$$

$$= \min\left(1, \exp(-\beta \Delta E)\right)$$

detailed balance?

suppose $E(\alpha_i) < E(\alpha_j)$

$P_{ij}\, a_j = P_{ji}\, a_i$ ← detailed balance condition

$\therefore \exp[-\beta(E(\alpha_i) - E(\alpha_j)]\cdot \exp(-\beta E(\alpha_j))$

$= \exp(-\beta E(\alpha_i)) \Rightarrow$ correct!

⇒ not strictly proved yet that this goes to $\exp(-\beta E)$ dist., only that dist is stationary

⇒ We have now constructed a Markov chain that will (after some time) give us the correct distribution! maybe exercise.

Pay attention: transition probs may be low

At low temp, Ising single flip idea:

↑↑↑↑↑↑↑ ----→ ↓↓↓↓↓↓↓

takes many unlikely steps

(so you should ensure good access, for instance by also flipping larger areas at once)

suppose slightly out of equilibrium:

$a_j + \epsilon$, $a_i - \epsilon$

$\Rightarrow a_j + \epsilon + P_{ji}\epsilon - P_{ij}\epsilon$, $a_i - \epsilon + P_{ij}\epsilon + P_{ij}\epsilon$

→ closer to equilibrium a_j, a_i

Nile example from F & S

misses the point! Metropolis not only samples just the nile, but also helps you find it.

Trial moves:

example: Ising model. flip a random spin.

Your Argon fluid: - continuous, not discrete phasespace
- kinetic term $\in$ get rid of this (integrate out) $\Rightarrow E = V$ see exercise

trial move = translation $\vec{r}_i' = \vec{r}_i + \Delta\vec{r}$

$\Delta\vec{r}$ ← random increment

random $x_i \in [0,1)$

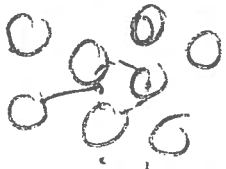
detailed balance, because reverse equally likely to be drawn

$$\Delta\vec{r} = \begin{pmatrix} \Delta\cdot(x_1 - 0{,}5) \\ \Delta\cdot(x_2 - 0{,}5) \\ \Delta\cdot(x_3 - 0{,}5) \end{pmatrix}$$

(or something)

How big should Δ be? Move all or one particle?
Answer: depends on situation. Whatever gets you eg. fastest.
(don't want too many rejections)

dense fluid



reject

gas

acceptable

$\Rightarrow$ Δ not too big at liquid densities

few or many particles

← cheaper to calculate ΔV

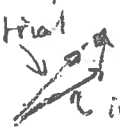
optimise $(\Sigma\Delta r)^2/t$ ← mean square displacement, computation time

people say, acceptance prob should be about ½
(bit more subtle)
f.e. if rejected moves are less work to calculate ← early rejection example should go here (forward page 34)

Internal d.o.f.

be careful, easy to bias and break detailed balance.

f.e. orientation of N_2



add random vector and normalise to get new orientation vector, → on unit sphere. (see FLS for how)

more complex orientation is trickier.

bond stretching, bending, torsion etc.

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
  ⇒ not so efficient.

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

end lecture 11

Important point: trial moves need not be physical (unlike MD)

as long as the reverse has same prob ⇒ detailed balance

Cluster moves.

Remember Ising model at low T, ↑↑↑↑↑↑ ↓↓↓↓↓↓

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

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

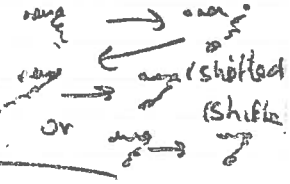
(common problem in MC & MD)

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

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

or tune acceptance probs

example: moving c.o.m of molecule



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example: Ising model.

↑−↑×↓×↓ etc. $H = -\sum_{nn} J S_i S_j$

↑×↓×↑×↓ ↑ assume positive.

$U = (N_a - N_p) J$

anti-parallel # parallel

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

generate same set of clusters from other config

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

$U' = U - 2J\Delta$

connected spins: p^{n_c}; broken spins: $(1-p)^{N_p - n_c}$

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

backward move

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

violate detailed balance?

$n_c' = n_c$ must flip same cluster back