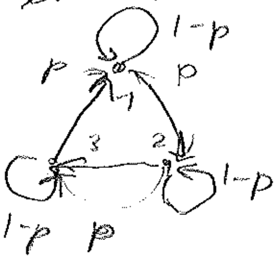
example ②



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

(compare to

$\Rightarrow$ no balance ③)

approach equilibrium?
if $p \neq 0, 1$, then let's look at sequence $\hat{a}(1) \ldots \hat{a}(n)$

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

don't write, too much work

$$(\hat{a}(n)-a)^2 = (1-p)^2\hat{a}_1(n-1)^2 + p^2\hat{a}_3(n-1)^2$$
$$+2(1-p)p\,\hat{a}_1\hat{a}_3 + \frac{1}{3}^2 - \frac{2}{3}\left[(1-p)\hat{a}_1 + p\hat{a}_3\right]$$
$$+$$

$$(\hat{a}(n)-a)^2 = \left((1-p)^2+p^2\right)\left(\hat{a}_1^2+\hat{a}_2^2+\hat{a}_3^2\right)$$
$$+ 2p(1-p)\left[\hat{a}_1\hat{a}_2+\hat{a}_1\hat{a}_3+\hat{a}_2\hat{a}_3\right] + \frac{1}{3} - \frac{2}{3}\left(\hat{a}_1+\hat{a}_2+\hat{a}_3\right)$$

strict if $a_1 \neq a_2 \neq a_3$, $a_1 \neq a_3$

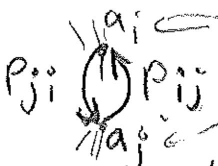
$$\leq \ldots + 2p(1-p)\left[\hat{a}_1^2+\hat{a}_2^2+\hat{a}_3^2\right] + \frac{1}{3} - \frac{2}{3}\left(\hat{a}_1+\hat{a}_2+\hat{a}_3\right)$$
$$= \hat{a}_1^2+\hat{a}_2^2+\hat{a}_3^2 + \frac{1}{3} - \frac{2}{3}\left(\hat{a}_1+\hat{a}_2+\hat{a}_3\right)$$
$$= \left(\hat{a}_1-\frac{1}{3}\right)^2 + \left(\hat{a}_2-\frac{1}{3}\right)^2 + \left(\hat{a}_3-\frac{1}{3}\right)^2 = \left(\hat{a}(n-1)-a\right)^2$$

$\Rightarrow$ convergence!

<u>detailed</u> balance
locally in balance

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

the same flow both ways
(<u>microreversibility</u>)



equilibrium populations

example ③ above does not have <u>detailed</u> balance, but just balance
example ① has detailed balance
strictly, only balance sufficient, but detailed balance more practical and not slower

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

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

② accept with p_{ji} probability with

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

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

detailed balance?

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

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

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

$= \exp(-\beta E(\alpha_i))$ ⇒ 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 give us (<u>after some time</u>) the correct distribution! maybe exercise.

Pay attention: transition probs may be low

At low temp, Ising single flip idea:

$\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow\uparrow \dashrightarrow \downarrow\downarrow\downarrow\downarrow\downarrow\downarrow$

takes many unlikely steps

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

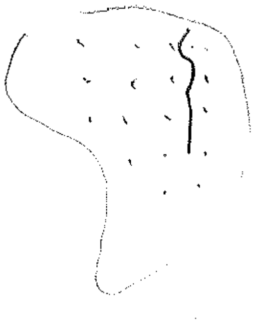
suppose slightly out of equilibrium:

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

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

→ 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 ← get rid of this (integrate out)
$\Rightarrow E = U$ see exercise

trial move = translation $\vec{r}_1' = \vec{r}_1 + \vec{\Delta r}$
random increment

random $x_i \in [0,1)$

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

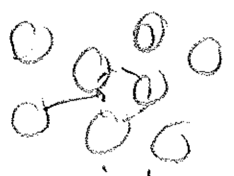
(or something)

detailed balance, because reverse equally likely to be drawn

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

end lecture 9

dense fluid



reject

gas

acceptable

$\Rightarrow$ Δ not too big at liquid densities

few or many particles
cheaper to calculate ΔU

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

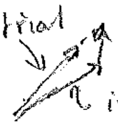
people say, acceptance prob should be about ½
(bit more subtle)
f.e. if rejected moves are less work to calculate ← early rejection example should go here (from page 34)

Internal d.o.f.

be careful, easy to bias and break detailed balance.

f.e orientation of N_2

trial



initial

add random vector and normalise to get new orientation vector.
→ on unit sphere.
(see F&S for how)

more complex orientation is trickier.