Error estimation:

Usual procedure: repeat expt. or simulation N times

$$\rightarrow \langle x \rangle = \frac{1}{N}\sum x_i \qquad \sigma^2 = \frac{1}{N}\sum (x_i - \langle x \rangle)^2$$

Central Limit thm. $\Rightarrow$ estimate of the mean is

$$\langle x \rangle \pm \sigma/\sqrt{N}$$

This relies on the N measurements being "identically distributed independent" samples of the pdf of x.

In MC this would require N indep. simulations with different random # seeds $\rightarrow$ different sequences of states

Because successive MC steps are correlated: only small changes in the configuration from step to step.

$\rightarrow$ Want to estimate how long it takes for "decorrelation" to occur in a single MC run: τ steps say, then

$$\text{error} = \sigma/\sqrt{N/\tau} \qquad : N/\tau = \#\text{ indep. configurations}$$

How to get N_0:

(i) Measure "correlation function" directly

$$C_n = \langle (x_i - \langle x \rangle)(x_n - \langle x \rangle) \rangle$$

expect C_n decreases with n, say τ is where $|C_n| = \varepsilon \sigma^2$ for some $\varepsilon \ll 1$.

+ ensemble averaging

Works but requires long runs to see decay of C_n.

Block average method:

Divide the MC run into n_b blocks of length b, $N = n_b \cdot b$

compute $\langle x \rangle_{j,b} = \frac{1}{b} \sum_{n=1+(j-1)b}^{jb} x_n$

= avg. over j^{th} block of size b

Note $\frac{1}{n_b} \sum_{j=1}^{n_b} \langle x \rangle_{j,b} = \frac{1}{n_b b} \sum_{k=1}^{N} x_k = \langle x \rangle$

let $\sigma_b^2 = \frac{1}{n_b} \sum_{j=1}^{n_b} \left(\langle x \rangle_{j,b} - \langle x \rangle \right)^2$ = block variance

note $\sigma_1^2 = \frac{1}{N} \sum_{i=1}^{N} \left(\text{data } x_i - \langle x \rangle \right)^2$ = global variance

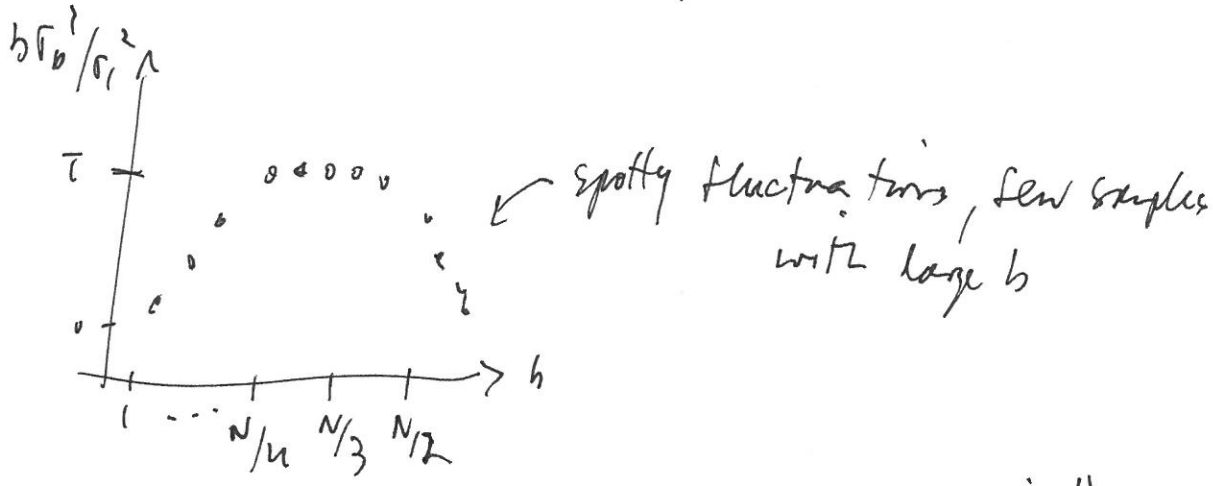
Idea: if $b \gg \tau$ the block averages are certainly uncorrelated and

$$\sigma_b^2 = \sigma_1^2 / (\#\text{ uncorrelated units})$$

$$= \sigma_1^2 / (b/\tau) = \sigma_1^2 \tau / b$$

or $\tau = \lim_{b \to \infty} \frac{b \sigma_b^2}{\sigma_1^2}$

In practice, can't let $N \to \infty$ so pick a large N & vary b from $1 \to N$ & look for a plateau:



Other analogous methods available { "jackknife" "bootstrap"

Ref: F+S Appendix D

Open ensembles

What's the Metropolis rule for the NpT ensemble where volume also varies?

pdf is $\propto e^{-(E+pV)/kT}$ in equilibrium

The key feature of the rule is that it satisfies detailed balance

$$\rho_i^{eq} \Pi_{i\to n} = \rho_n^{eq} \Pi_{n\to i}$$

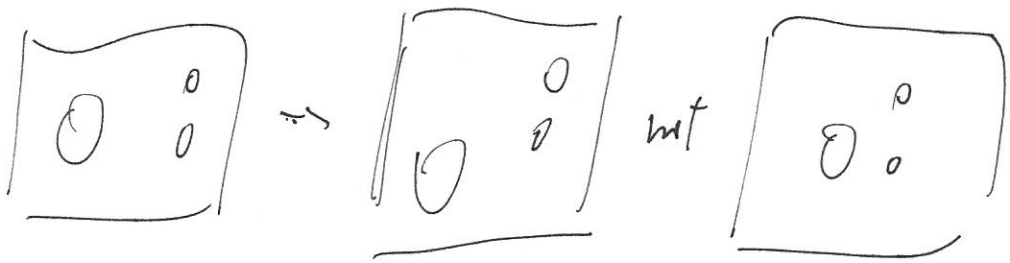
$$\Pi_{i\to n} = \alpha_{in} \gamma_{i\to n} \quad \text{take } \alpha_{in} = \alpha_{ni}$$

so $$\frac{\gamma_{i\to n}}{\gamma_{n\to i}} = \frac{\rho_n^{eq}}{\rho_i^{eq}} = e^{-(\Delta E + p\Delta V)/kT}$$

ΔE: old $\to$ new

Alternate btw. position shifts & volume changes.

ΔV: start



expanded/contracted system should be uniform so it's incorrect to just change $box \to box \pm \Delta box$, need to contract/dilate particle positions as well.

$\to$ use scaled variables $s_{ix} \equiv \frac{x_i}{box_x}$ $\quad 0 \le s_i < 1$

and vary box with $\{\underline{s}_i\}$ fixed - preserves uniformity

2 more things:

(1) $U = U(\{\underline{r}_i\}) = U(\{\text{box}\cdot\underline{s}_i\})$ so U changes as well

In general recomputing U is an $O(N^2)$ calculation, but for LJ (or power-law potentials) it's easier:

$$U_{LJ} = 4\varepsilon\left[\left(\frac{b\cdot s}{\sigma}\right)^{-12} - \left(\frac{b\cdot s}{\sigma}\right)^{-6}\right] \qquad b \equiv \text{box}$$

$$= b^{-12}\cdot 4\varepsilon\left(\frac{\rho}{s}\right)^{-12} - b^{-6}\cdot 4\varepsilon\left(\frac{\rho}{s}\right)^{-6}$$

So $\Delta U_{LJ} = (b'^{-12} - b^{-12})\cdot 4\varepsilon\sum_{i<j}\left(\frac{s_{ij}}{\sigma}\right)^{-12}$ ← save these separately

$$- (b'^{-6} - b^{-6})\cdot 4\varepsilon\sum_{i<j}\left(\frac{s_{ij}}{\sigma}\right)^{-6}$$

When b changes the sums do not - 2 calculations

(2) Recall the NpT pdf is

$$\frac{1}{Q_{NpT}} e^{-(U+pV)/kT} \int_{i=1}^{N} d^3r_i \cdot dV \qquad d^3r_i = V\, d^3s_i$$

$$= \frac{1}{Q_{NpT}} e^{-\underbrace{(U+pV - NkT\log V)/kT}_{\equiv \Sigma}} \int_1^N d^3s_i \, dV$$

So the Metropolis rule is: accept ΔV with probability

$$p = \min\{1, e^{-\Delta\Sigma/kT}\} \quad \text{not } \Delta U \text{ or } \Delta(U+pV)$$

MC for the Grand Canonical ensemble:

Here V + T are fixed but N varies! must add/remove particles

3 types of MC step: position shift, add or remove particle
could alternate or choose any with prob = 1/3
to insure $\alpha_{ij} = \alpha_{ji}$

Addition step: pick a location at random, accept a new particle there with prob = $\min\left\{1, \frac{zV}{N+1} e^{-(U_{N+1}-U_N)/kT}\right\}$ $z = e^{\beta\mu}$

Removal step: pick a particle at random & delete it
with prob = $\min\left\{1, \frac{N}{zV} e^{-(U_{N-1}-U_N)/kT}\right\}$

justify rules by D.B. again:

equil pdf is $\rho_{GCE}^{N}(\{r_i\}) = \frac{1}{N!}\left(\frac{V}{\lambda_{TH}^3}\right)^N e^{(\mu N - U_N)/kT} \prod_i d\{r_i\}$

so $\frac{\gamma_{N\to N+1}}{\gamma_{N+1\to N}} = \frac{\rho^{N+1}}{\rho^{N}} = \frac{zV}{N+1} e^{-(U_{N+1}-U_N)/kT} \equiv R$

$\rightarrow \gamma_{N\to N+1} = \min\{1, R\}$

$\gamma_{N+1\to N} = \min\left\{1, \frac{N+1}{zV} e^{-(U_N - U_{N+1})/kT}\right\} = \min\{1, R^{-1}\}$

so: if $R > 1$ $\gamma_{N\to N+1} = 1$
$\gamma_{N+1\to N} = R^{-1}$
} ratio $= R$

if $R<1$ $\quad \gamma_{N\to N+1} = R$, $\gamma_{N+1\to N} = 1$ } ratio $= R$

Often choices available, e.g. remove a particle with prob $= \frac{1}{1+R}$, create with prob $= \frac{1}{1+R'}$

Practical issue: if the density is high most insertions are at near a pre-existing particle, ΔU large, reject

Picking open regions not consistent with $\delta\mathbf{r}$.

Coding issue:

adding $\#(N+1)$ to $\{x(i), i=1\cdots N\}$ → long arrays } inefficient
removing $\#k$ from $\{$ " $\}$ → gaps } calculation

→ Use pointer array $\mathrm{loc}(i)$ $i=1,\cdots N,\cdots$

at start set $\mathrm{loc}(i)=i$ & refer to $x(\mathrm{loc}(i))$ not $x(i)$

Addition: $N \to N+1$

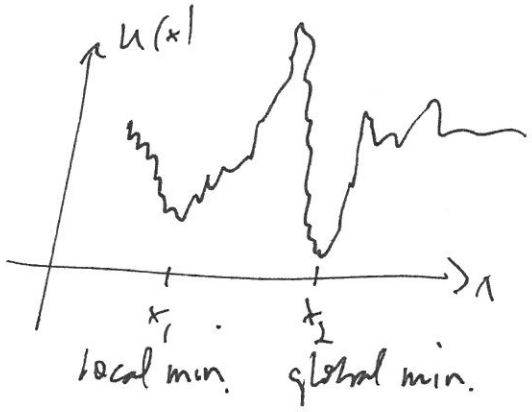
$\mathrm{loc}(N+1) = N+1$
$x(N+1) = x_{new}$
y :
z

Removal: do $i = k, N-1$
$\mathrm{loc}(i) = \mathrm{loc}(i+1)$
enddo
$N \to N-1$

Low temperature issues

x = some coordinate

$p_{eq}(x) \propto e^{-u(x)/kT}$



High T: $\Delta u/kT$ small, $e^{-\Delta u/kT} = O(1)$, lots of MC moves
→ good sampling of phase space

Low T: $\Delta u/kT$ large, $e^{-\Delta u/kT}$ small, few transitions ($1 \leftrightarrow 2$)
→ trapped in nearby min region
could miss global min states

Brute force fix - take large steps & be patient

Annealing: lower T gradually
high T: all x sampled
medium T: minima favored
low T: global min favored

pdf gradually adjusts to T

drawback: contributions of other local minima omitted.

Best when focus is on global min state

e.g. traveling salesman problem - E = total length
pick a route, get E, switch to get E', use Metropolis
... Ensemble avg. as a check.

Replica exchange:

simulate 2 copies of the system at high T_1 & low T_2, and switch the T_i while keeping the state the same.

The T_1 simulation samples all x and if $T_1 \to T_2$ at various values of old x_1 = new x_2, the full range of x_2 will be sampled as well.

Need DB to insure the correct ρ_{eq} for both systems.

3 MC modes: usual MC in the T_1 system

" " T_2 "

$\beta = \frac{1}{kT}$ switch T_1 & T_2 with prob $= \min\{1, e^{\Delta\beta\Delta E}\}$

Proof: The combined 1+2 system has pdf

$$\rho_{ij}(\beta_1,\beta_2) = \text{prob}\{1 \text{ is in state } i \text{ at } T_1 \text{ and } 2 \text{ is in state } j \text{ at } T_2\}$$

$$= \frac{1}{Q_1 Q_2} e^{-\beta_1 E_{1i} - \beta_2 E_{2j}}$$

because 1 & 2 do not interact

$$\frac{\pi(\beta_1 E_{1i}, \beta_2 E_{2j} \to \beta_2 E_{1i}, \beta_1 E_{2j})}{\pi(\beta_2 E_{1i}, \beta_1 E_{2j} \to \beta_1 E_{1i}, \beta_2 E_{2j})} = \frac{\rho_{eq}(\beta_2 E_{1i}, \beta_1 E_{2j})}{\rho_{eq}(\beta_1 E_{1i}, \beta_2 E_{2j})}$$

$$= \frac{e^{-\beta_2 E_{1i} - \beta_1 E_{2j}}}{e^{-\beta_1 E_{1i} - \beta_2 E_{2j}}} = e^{(\beta_2 - \beta_1)(E_{2j} - E_{1i})}$$

$$= e^{\Delta\beta \cdot \Delta E} \equiv R$$

→ claim $\text{prob}(T_1 \leftrightarrow T_2) = \min\{1, R\}$

pf: $$\frac{\text{prob}(\beta_1 E_1, \beta_2 E_2 \to \beta_2 E_1, \beta_1 E_2)}{\text{prob}(\beta_2 E_1, \beta_1 E_2 \to \beta_1 E_1, \beta_2 E_2)} = \frac{\min(1, R)}{\min(1, 1/R)}$$

if $R > 1$ num = 1, den = $1/R$, ratio = R ✓

if $R < 1$ num = R, den = 1, ratio = R

$- + -$

Idea: Here $T_1 \gg T_2$ so $\beta_1 \ll \beta_2$, $\Delta\beta < 0$

Typically $E_1 > E_2$ so $\Delta\beta\Delta E < 0$ → reject

But, if #1 happens to be in a low-E state

(not unlikely because #1 samples x wall)

ΔE can be small or < 0 → accept

How often to switch: when there's a new configuration in #1 → every decorrelation time τ_1.

Improvement – parallel tempering

T-flips still not so likely if $T_2 \ll T_1$ so instead look at N copies $\beta_1 < \beta_2 < \beta_3 < \cdots < \beta_N$

(high T … low T)

↑ switch between i and $i \pm 1$ only, $|\beta_i - \beta_{i\pm1}|$ smaller

Needs a parallel platform.

Free energy: $F = -kT \log Z$ but Z not calculable

Method I: based on calc of μ in an NVT simulation

recall $E = TS - pV + \mu N$ from previous lecture

$\rightarrow$ $F = E - TS = -pV + \mu N$

NVT sim: $\langle F \rangle = -\langle p \rangle V + \langle \mu \rangle N$

($\langle p \rangle$: calc, V: known, $\langle \mu \rangle$: calc, N: known)

(GCE sim: $\langle F \rangle = -\langle p \rangle V + \mu \langle N \rangle$ if μ known)

Notice $Z_N = \frac{1}{\Lambda_{tm}^{3N} N!} \int \prod_{i=1}^{N} d^3 r_i \, e^{-U_N/kT}$

$$U_{N+1} = U_N + \sum_{j=1}^{N} U_{j,N+1} = U_N + \Delta U$$

$$\Rightarrow \frac{Z_{N+1}}{Z_N} = \frac{1}{\Lambda_{tm}^3 (N+1)} \int \prod_{i}^{N} d^3 r_i \, e^{-U_N/kT} \cdot \int d^3 r_{N+1} \, e^{-\Delta U/kT}$$

$$\frac{\int \prod_{i}^{N} d^3 r_i \, e^{-U_N/kT}}{}$$

$$= \frac{V}{\Lambda_{tm}^3 (N+1)} \left\langle \int \frac{d^3 r_i}{V} e^{-\Delta U/kT} \right\rangle_{NVT}$$

While $\mu = \left(\frac{\partial F}{\partial N}\right)_{VT} \rightarrow \frac{F_{N+1} - F_N}{T} = -kT \log \frac{Z_{N+1}}{Z_N}$

so $\mu = -kT \log \frac{V}{\Lambda^3 (N+1)} - kT \log \int \frac{d^3 r_{N+1}}{V} \langle e^{-\Delta U/kT} \rangle$

$= \mu_{IG}^{\top} \mu_{ex}$ $\qquad \mu_{IG} = \mu_{IG}(N+1, V, T) \cong \mu_{id}(NVT)$

μ_{ex}: pick a random uniformly-distributed point in V: $\int \frac{d^3 r_{N+1}}{V}$

evaluate the ΔU for a "virtual particle" at $\underline{r}_{N+1}$, which does not effect the dynamics of the other N particles

average over an NVT ensemble

Works well if the density isn't too high, otherwise $\underline{r}_{N+1}$ is likely to be near another particle $\Rightarrow$ high $\Delta U \Rightarrow$ reject

long range tail correction:

$$\mu_{tail} = -kT \log \int_{|\underline{r}_{N+1} - \underline{r}_i| > r_c} \frac{d^3 r_{N+1}}{V} \underbrace{\langle e^{-\Delta U/kT} \rangle}_{\cong 1 - \Delta U/kT \text{ here}}$$

$$= -kT \int_{r_c}^{\infty} \frac{4\pi r^2 dr}{V} \Delta U \cdot g(r)$$

Particle deletion?

$$\mu = +kT \log \frac{Z_N}{Z_{N+1}} \qquad \text{(flip the log)}$$

$$= kT \log (N+1) \Lambda_{TH}^3 V \; \frac{\int \prod_1^N d^3 r_i \, e^{-U_N/kT} \int \frac{d^3 r_{N+1}}{V} e^{-\Delta U/kT} \cdot e^{+\Delta U/kT}}{\int \prod_1^{N+1} d^3 r_i \, e^{-(U_N + \Delta U)/kT}}$$

$$= kT \log (N+1) \Lambda_{TH}^3 V \; \underbrace{\left\langle \int \frac{d^3 r_{N+1}}{V} e^{+\Delta U/kT} \right\rangle_{(N+1)VT}}_{\text{"unstable" integral}}$$