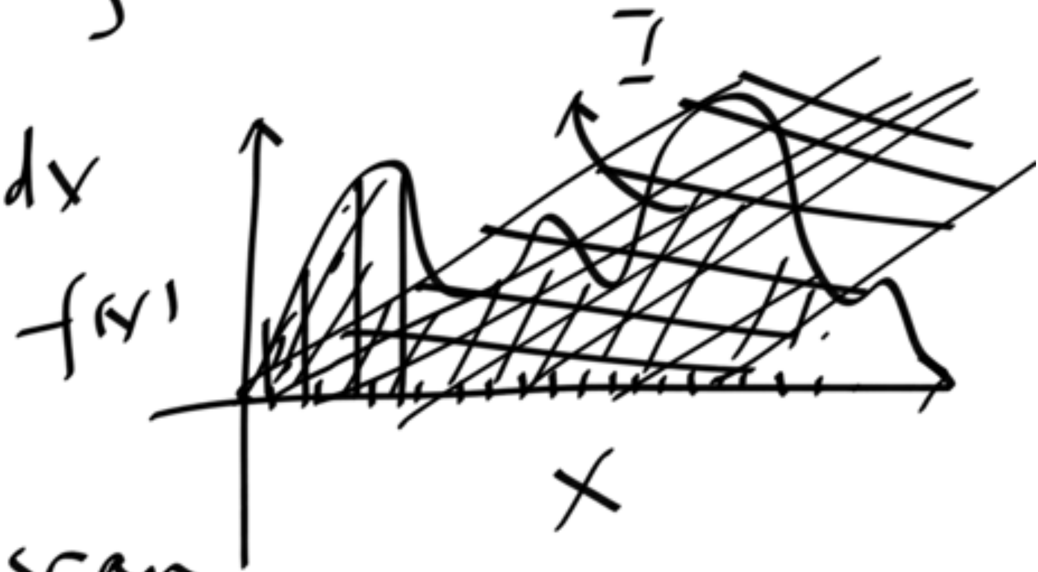
$$\langle A\rangle = \underbrace{\frac{\int A(\ \vec{q}) e^{-\beta H(\vec{p},\vec{q})} \, d\vec{p}\, d\vec{q}}{\int e^{-\beta H(\vec{p},\vec{q})} \, d\vec{p}\, d\vec{q}}}_{f(\vec{q},\, \vec{p})}$$

$$I = \int_a^b f(x)\, dx$$



<u>systematic scan</u>

$$\frac{5^{300}}{52^{300}}$$

$$I = \int_a^b f(x)\,dx = (b-a)\langle f(x)\rangle$$

$$= (b-a)\frac{1}{L}\sum_{i=1}^{L} f(x_i)$$

$x \in [a, b]$
uniform

There could be many ways of sampling x. The simplest one is called random sampling, namely x is uniformly distributed between a and b. However, this sampling approach has issue of large statistical errors in the case that the singificant values of the funtion is sparsely distributed.

Now let us sample x by following the distribution w(x)

$$I = \int_a^b f(x)\,dx$$

$w(x)$

According to normalization condition

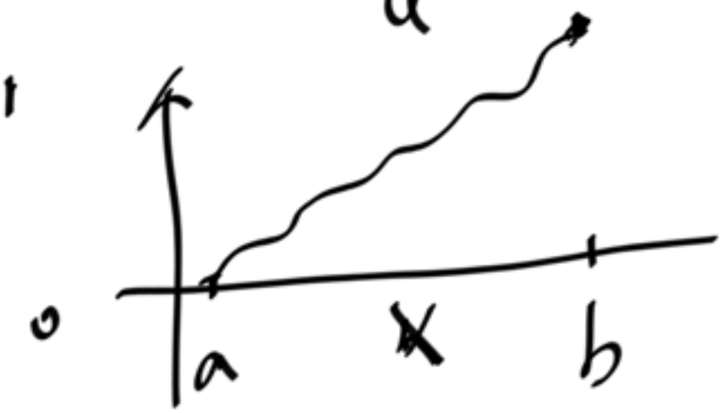
$$\int_a^b w(x)\,dx = 1$$

$$= \int_a^b \frac{f(x)}{w(x)} \cdot \underline{w(x)\,dx}$$

Define u(x) as

$$u(x) = \int_a^x w(x')\,dx'$$

$$= \int_a^b \frac{f(x)}{w(x)} \underbrace{\frac{\partial u(x)}{\partial x} \cdot \cancel{dx}}_{du}$$



Change variable from x to u

$$= \int_0^1 \frac{f(x(u))}{w(x(u))} \cdot du$$

$$\frac{\partial u(x)}{\partial x} = w(x)$$

$$= \underline{\frac{1}{L} \sum_{i=1}^{L} \frac{f(x(u_i))}{w(x(u_i))}}$$

$$I_0 = \left\langle \frac{f}{w} \right\rangle$$

$I_1, \; I_2, \; \ldots$

$$\sigma_I^2 = \langle (I - I_0)^2 \rangle$$ over many measurements.

$$= \langle (I - I_0)(I - I_0) \rangle$$

$$= \left\langle \frac{1}{L^2} \sum_{i=1}^{L} \sum_{j=1}^{L} \left(\frac{f(x(u_i))}{w(x(u_i))} - I_0 \right) \times \left(\frac{f(x(u_j))}{w(x(u_j))} - I_0 \right) \right\rangle$$

$$\frac{f(x(u_i))}{w(x(u_i))} \sim f/w(i)$$

$$= \frac{1}{L^2} \sum_{i}^{L} \sum_{j}^{L} \langle (f/w(i) - I_0)(f/w(j) - I_0) \rangle$$

$$= \frac{1}{L^2} \sum_{i} \sum_{j} \langle f/w(i) \cdot f/w(j) - \underbrace{I_0 (f/w(i) + f/w(j))}_{\text{II}} + \underbrace{I_0^2}_{\text{III}} \rangle$$

$$\frac{1}{L^2}\sum_i\sum_j \langle f_w(i)\, f_w(j)\rangle$$

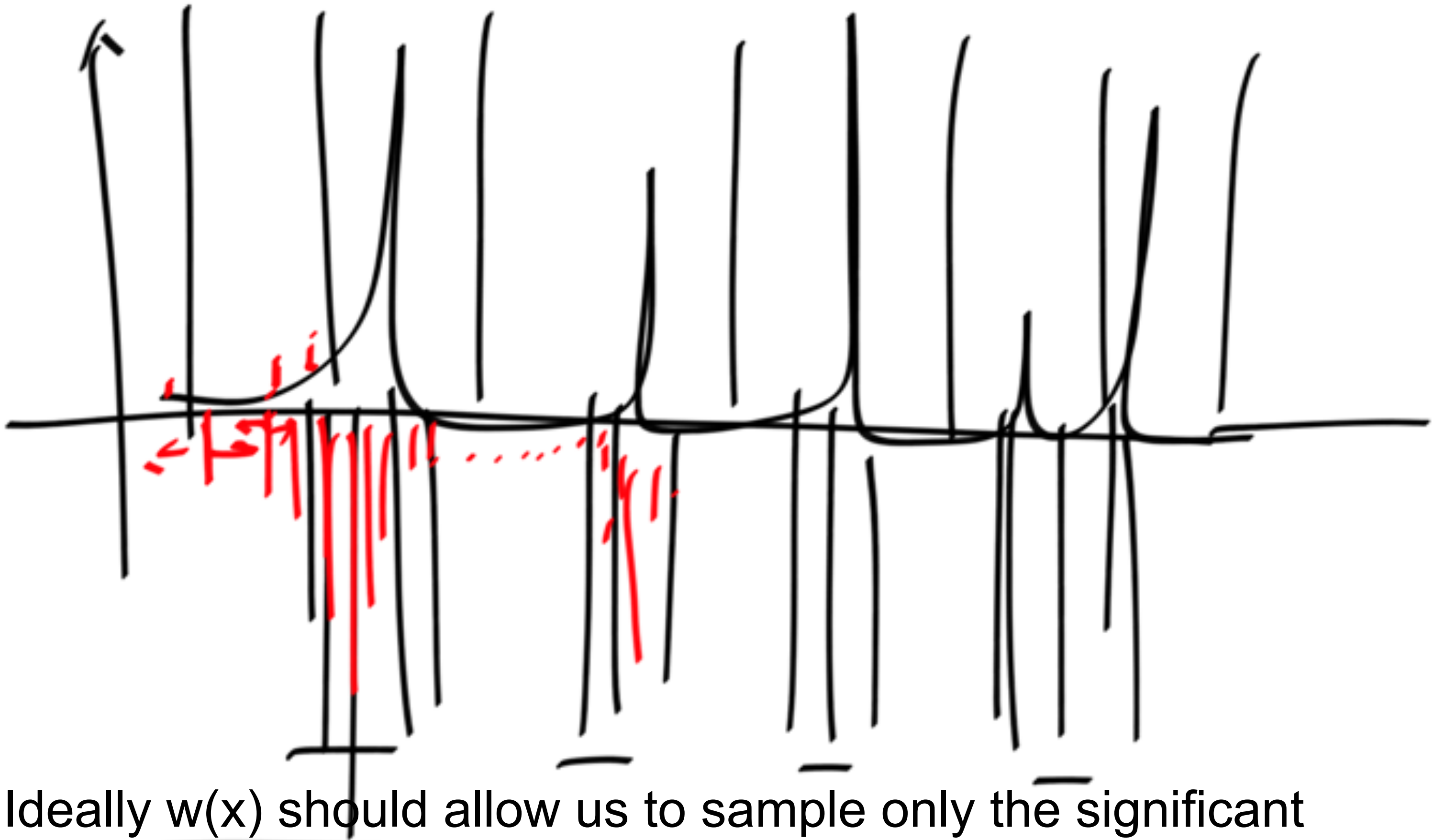
$$\frac{1}{L^2}\sum_{i\neq j}\underbrace{\langle f_w(i)\rangle}_{I_0}\underbrace{\langle f_w(j)\rangle}_{I_0} \rightarrow \frac{1}{L^2}L(L-1)I_0^2$$

$$+\frac{1}{L^2}\sum_i \langle f_w(i)^2\rangle = \frac{1}{L^2}\cdot L\cdot\langle f_w^2\rangle$$

(II) $\frac{1}{L^2}\left(-2L^2 I_0^2\right)$ (III) : $\frac{1}{L^2}\cdot L^2 I_0^2$

$$\sigma_I^2 = \frac{1}{L}\left[\langle f_w^2\rangle - \langle f_w\rangle^2\right]$$

Average over many measurements which give rise to true values



Ideally w(x) should allow us to sample only the significant region of x

Metropolis Method:

$\vec{o} \in \mathbb{R}^{3N}$

$\vec{n} \leftarrow \vec{o} + \vec{\delta}$

acceptance prob: $\pi(\vec{o} \rightarrow \vec{n})$

Given these are M walkers sampling the system (M is a very large number)

$$M$$

$$\frac{m(\vec{o})}{M} \propto p(\vec{o}) = \frac{e^{-\beta U(q)}}{Z}$$

When sampling is converged, at any given moment, the number of the walkers that happen to visit configuration O is m(O)

$$\sum_{n} \underbrace{M p(\vec{o})}_{m(\vec{o})} \pi(\vec{o} \to \vec{n})$$

To ensure m does not change over subsequent sampling iteration, one needs to ensure

$$= \sum_{\vec{n}} m(\vec{n}) \pi(\vec{n} \to \vec{o})$$

A sufficient but not necessary condition : detailed balance

$$\left.\begin{aligned} &\sum_{\vec{n}} p(\vec{o}) \pi(\vec{o} \to \vec{n}) \\ &= \sum_{n} p(\vec{n}) \pi(\vec{n} \to \vec{o}) \end{aligned}\right\}$$

$$p(\vec{o}) \pi(\vec{o} \to \vec{n}) = p(\vec{n}) \pi(\vec{n} \to \vec{o})$$

$\hookrightarrow$ detailed balance.

$$\frac{\pi(\vec{o}\to\vec{n})}{\pi(\vec{n}\to\vec{o})} = \frac{p(\vec{n})}{p(\vec{o})}$$

$$= e^{-\beta(U(\vec{n})-U(\vec{o}))}$$

Prob to generate movement

$$\pi(\vec{o}\to\vec{n}) = \alpha(\vec{o}\to\vec{n})\,acc(\vec{o}\to\vec{n})$$

Prob to accept the generated movement

$$\frac{acc(\vec{o}\to\vec{n})}{acc(\vec{n}\to\vec{o})} = \frac{\alpha(\vec{n}\to\vec{o})}{\alpha(\vec{o}\to\vec{n})}\frac{p(\vec{n})}{p(\vec{o})}$$

$$\Updownarrow$$

$$= \frac{p(\vec{n})}{p(\vec{o})} = e^{-\beta(U(\vec{n})-U(\vec{o}))}$$

$$acc(\vec{o}\to\vec{n}) = \min\left(1, e^{-\beta(U(\vec{n})-U(\vec{o}))}\right)$$

A general MOnte Carlo procedure

① Randomly select a/several particle(s)

Calculate energy $\mathcal{U}(\vec{o})$

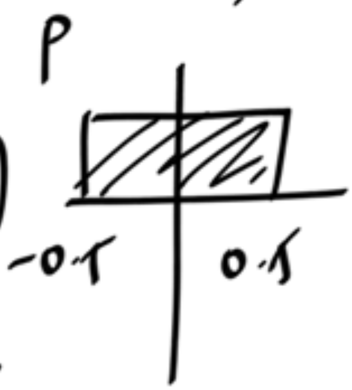
② $\vec{n} = \vec{o} + \underline{\vec{\Delta}}$

③ evaluate $\mathcal{U}(\vec{n})$, calculate

$e^{-\beta \Delta \mathcal{U}}$

④ acc or reject according to $\min(1, e^{-\beta \Delta \mathcal{U}})$

$\vec{\Delta}$: $a \cdot b$ $\quad b \in [-0.5, 0.5]$



$b \in [-0.3, 0.7]$

>0.3

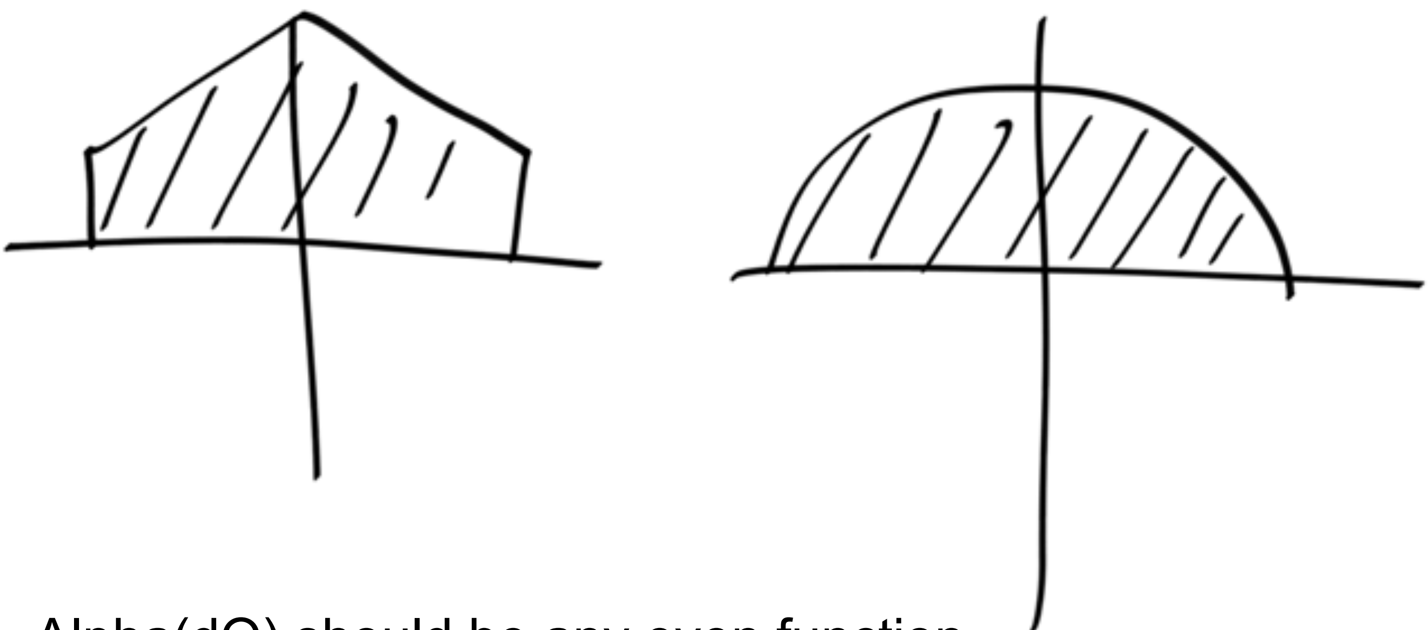
$$\alpha(\vec{o} \to \vec{n}) = \alpha(\vec{n} \to \vec{o})$$

$$\alpha(\vec{o} \to \overbrace{\vec{o} + [0.3, 0.7]}^{n}) \propto P$$

$$\alpha(\vec{o} \to \vec{o} - [0.3, 0.7]) = 0$$

$$\alpha(\vec{n} \to \vec{o}) = 0$$

$$\alpha(\vec{o} \to \vec{n}) \neq \alpha(\vec{n} \to \vec{o})$$



Alpha(dO) should be any even function

A given amount of computation power , how large the conformational space can be explored

all accepted movements

$$\left\langle \sum_i \Delta \underline{q}_i^2 \right\rangle_{\Delta q} =$$

$$\int_{-\infty}^{+\infty} d\Delta \underline{q} \int \frac{e^{-\beta U(\underline{q})}}{Z} \cdot \pi(\underline{q}, \underbrace{\underline{q}+\Delta \underline{q}}) \cdot \Delta \underline{q}^2 \, d\underline{q}$$

$p(\Delta \underline{q})$

$$= \underbrace{\langle \Delta \underline{q}^2 \rangle_{\Delta q, q} \cdot \underline{N}} = \left\langle \sum \Delta \underline{q}_i^2 \right\rangle_{\Delta q}$$

$$\underline{\langle \underline{\pi(\underline{q}, \underline{q}+\Delta \underline{q})} \Delta \underline{q}^2 \rangle_{\Delta q, q}} \sim \langle \Delta \underline{q}^2 \rangle_{\Delta q, q}$$

$$e^{-\beta \left[U(\underline{q}+\Delta \underline{q}) - U(\underline{q}) \right]}$$

$$\underline{\langle U(\underline{q}+\Delta \underline{q}) - U(\underline{q}) \rangle \sim k_B T}$$

$$\left\langle U(\vec{q}+\Delta\vec{q}) - U(\vec{q}) \right\rangle = k_B T$$

$$U(\vec{q}+\Delta\vec{q}) - U(\vec{q})$$

$$U(q_1 + \Delta q_1, q_2 + \Delta q_2, \ldots) - \underbrace{U(q_1, q_2 \ldots q \ldots)}$$

$$= \left(\frac{\partial U(\vec{q})}{\partial q_1}\right)_{q_2 q_3 \ldots} \Delta q_1 + \cdots + \left(\frac{\partial U(\vec{q})}{\partial q_i}\right)_{\ldots q_{i-1}, q_{i+1}, \ldots} \Delta q_i$$

$$+ \frac{1}{2}\left(\frac{\partial^2 U(\vec{q})}{\partial q_1^2}\right)\Delta q_1^2 + \ldots \ldots$$

$$N(N-1)$$

$$+ \frac{1}{2}\left(\frac{\partial^2 U(\vec{q})}{\partial q_1 \partial q_2}\right)\Delta q_1 \Delta q_2 + \ldots \ldots$$

$$+\left(\qquad\right)\Delta \underline{q}_i^3 + \cdots$$

$$\left(\qquad\right)\Delta \underline{q}_i^2 \Delta \underline{q}_j + \cdots$$

$$\left(\qquad\right)\Delta \underline{q}_i \Delta \underline{q}_j \Delta \underline{q}_k + \cdots$$

$$+ O(\Delta \underline{q}_i^4) \quad \underbrace{\langle U(\vec{\underline{q}}+\Delta \vec{\underline{q}}) - U(\vec{\underline{q}}) \rangle_{\Delta \underline{q}, \underline{q}}}_{\text{all at once}}$$

$$\left\langle \frac{\partial U(\underline{q})}{\partial \underline{q}_i} \Delta \underline{q}_i \right\rangle_{\Delta \underline{q}, \underline{q}}$$

$$\underbrace{\left\langle \frac{\partial U(\underline{q})}{\partial \underline{q}_i} \right\rangle_{\underline{q}}} \underbrace{\langle \Delta \underline{q}_i \rangle_{\Delta \underline{q}}}^{=0}$$

$$\langle \delta q_i \, \delta q_j \rangle_{\delta q_i} = \langle \delta q_i \rangle_{\delta q} \langle \delta q_j \rangle_{\delta q} = 0$$

$i \neq j$

$$\langle \delta q_i^2 \rangle_{\delta q, q}$$

$$\underset{\substack{\vee \\ k_B T}}{\langle U(q+\delta q) - U(q) \rangle_{\delta q, q}} = \sum_i \overbrace{\frac{1}{2}\left\langle \frac{\partial^2 U}{\partial q_i^2} \right\rangle}^{N} \langle \delta q_i^2 \rangle + \underbrace{O(\delta q_i^4)}_{\approx 0}$$

$f(u)$

$$N \cdot f(u) \langle \delta q^2 \rangle = k_B T$$

$\rightarrow$ total displacement

$$N\langle \delta q^2 \rangle = \frac{k_B T}{f(u)}$$

n sites : nN

$$\text{eff} = \frac{k_B T}{nNf(u)}$$

$$\Big\langle U(\underline{q}_1, \underline{q}_2, \ldots \underline{q}_i + \Delta\underline{q}_i \ldots) - U(\underline{q}_1, \underline{q}_2 \ldots \underline{q}_i \ldots) \Big\rangle = \underline{k_B T}$$

$$= \frac{\frac{1}{2}\left\langle \frac{\partial^2 U}{\partial \underline{q}_i^2} \right\rangle}{f(n)} \langle \Delta q^2 \rangle \quad + O(\Delta \underline{q}^4)$$

tot disp: $\quad \alpha \cdot \langle \Delta q^2 \rangle = \frac{NkT}{f(u)}$

eff: $\quad \frac{NkT}{f(n)} \cdot \frac{1}{nN} = \cancel{kT/nf(u)}$

$$\frac{\partial \langle E \rangle}{\partial \beta} = -\left(\langle E^2 \rangle - \langle E \rangle^2\right)$$

$$\hookrightarrow \quad k_B T^2 \cdot \underbrace{\left(\frac{\partial \langle E \rangle}{\partial T}\right)_{V,N}}_{C_V} = \underline{\langle E^2 \rangle} - \langle E \rangle^2$$

$$E = \underline{\underline{U}} + \underline{\underline{K}}$$

$$k_B T^2 \frac{\partial \langle U + K \rangle}{\partial T} \rightarrow k_B T^2 \cdot \frac{\partial \left(\langle U \rangle + \langle K \rangle\right)}{\partial T}$$

$$\Rightarrow k_B T^2 \left(\underline{\frac{\partial \langle U \rangle}{\partial T}} + \frac{3}{2} N k_B \right)$$

$$k_B T^2 \frac{\partial \langle U \rangle}{\partial T} = \langle U^2 \rangle - \langle U \rangle^2$$

$$\underbrace{\partial T}_{\hookrightarrow C_{V,pot}}$$

$$C_V = C_{V,pot} + \frac{3}{2} N k$$

$$\frac{acc(\vec{o} \to \vec{n})}{acc(\vec{n} \to \vec{o})} = e^{-\beta(U(\vec{n}) - U(\vec{o}))}$$

$$P(\vec{o}) \propto e^{-\beta U(\vec{o})} / Z$$

$$P(\vec{n}) \propto e^{-\beta U(\vec{n})} / Z$$

$$P(\vec{o})\, \underline{\alpha(\vec{o} \to \vec{n})}\, \underline{acc(\vec{o} \to \vec{n})}$$

$$P(\vec{n}) \cdot \underline{\alpha(\vec{n} \to \vec{o})}\, \underline{acc(\vec{n} \to \vec{o})}$$

(N, V, E)

$$E = U + \underbrace{K}_{\geq 0}$$

① generate new conf $\vec{n} = \vec{o} + \vec{\delta}$

$$\Delta U = U(\vec{n}) - U(\vec{o})$$

if $\Delta U < 0$, accept

$$K \leftarrow |\Delta U|$$

if $\Delta U > 0$;

if $K \geq \Delta U$: accept

$$K \rightarrow \Delta U$$

else: reject.

Isobaric – Isothermic Ensemble.

NPT

$$\ln \sum_{V} \sum_{E} \Omega(N,V,E)\, e^{-\beta E} e^{-\beta P V} = \beta T S - \beta E - \beta P V$$

$$\underset{NPT,\ \underline{PF}}{\underline{\Delta}} = \sum_{V} \underline{Q(N,V,T)}\, e^{-\beta P V} = -\beta G$$

$$\Delta = \beta P \int dV \cdot e^{-\beta P V} \cdot \frac{1}{\Lambda^{3N} \cdot N!} \int e^{-\beta U(q_n)} \cdot dq_n$$

$$\underline{q_n} = \underline{L} \cdot S_n\,(0 \,..\, 1)$$

$$L^3 \to V$$

$$\Delta = \beta P \int dV\, e^{-\beta P V}\, V^N \int_0^1 ds_N \cdot e^{-\beta \underbrace{U(s_N, L)}_{U(q_N)}}$$

$$\begin{cases} \rho(V, \vec{s}_N) \\ \propto V^N \cdot e^{-\beta P V} \cdot e^{-\beta U(s_N, L(V))} \end{cases} \qquad U(s_N, L(V))$$

$$V \longrightarrow V + \Delta V \qquad [-\Delta V_{max}, +\Delta V_{max}]$$

$$\begin{cases} \rho(V, \vec{s}_N)\, \pi(V \to V + \Delta V) \\ = \underline{\rho(V + \Delta V, \vec{s}_N)\, \pi(V + \Delta V \to V)} \end{cases}$$

$$\pi(V \to V + \Delta V) = \alpha(V \to V + \Delta V) \cdot acc(V \to V + \Delta V)$$

$$P(V, S_N)\, acc(V \to V+\Delta V) = P(V+\Delta V, S_N)\, acc(V+\Delta V \to V)$$

$$\frac{acc(V \to V+\Delta V)}{acc(V+\Delta V \to V)} = \frac{P(V+\Delta V, S_N)}{P(V, S_N)}$$

$$P(V) = e^{-\beta\left(\mathcal{U}(\vec{s}_N, L) + PV - \underbrace{N\beta^{-1}\ln V}\right)}$$

$$V^N = e^x \qquad \underline{N \ln V} = x$$

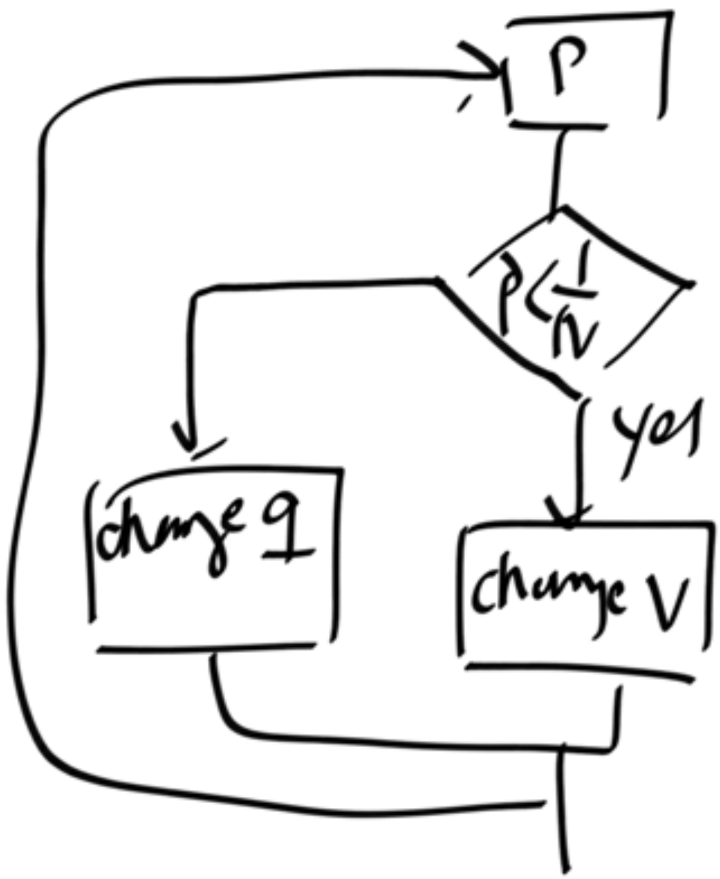
$$\to \min\left(1,\ e^{-\beta\left[\mathcal{U}(\vec{s}_N, L(V+\Delta V)) - \mathcal{U}(\vec{s}_N, \bar{L}(V)) + \underline{P}\Delta V - \underline{N}\beta^{-1}\ln\frac{V+\Delta V}{V}\right]}\right)$$

Do we need to re-evaluate pairwise interaction for volume change ?

$$U = \sum_{n=1}^{m} \sum_{i<j} \epsilon \left(\frac{\sigma_n}{r_{ij}}\right)^n$$

$$L \rightarrow L'$$

$$U_n(L') = \left(\frac{L}{L'}\right)^n \cdot U_n(L)$$



$$\bar{P} = \sum_i P_i e^{-\beta E_i}$$

$$A = E - TS \qquad A = -\beta^{-1} \ln Q$$

$$Q = e^{-\beta A}$$

$$dA = dE - d(TS)$$

$$\partial e^x$$

$$= T\,dS - P\,dV - d(TS) \qquad = e^x \cdot \partial x$$

$$= -S\,dT - \bar{P}\,dV$$

$$\bar{P}(V) = -\left(\frac{\partial A}{\partial V}\right)_{N,T} \qquad P$$

$$\langle \bar{P}(V) \rangle_V = \frac{\beta P}{\Delta} \int_0^\infty dV \left(-\frac{\partial A}{\partial V}\right)_{N,T} e^{-\beta A} \quad e^{-\beta PV}$$

$$= \frac{P}{\Delta}\int_0^\infty \underbrace{dV \left(\frac{\partial e^{-\beta A}}{\partial V}\right)}_{A} \cdot \underbrace{e^{-\beta PV}}_{B}$$

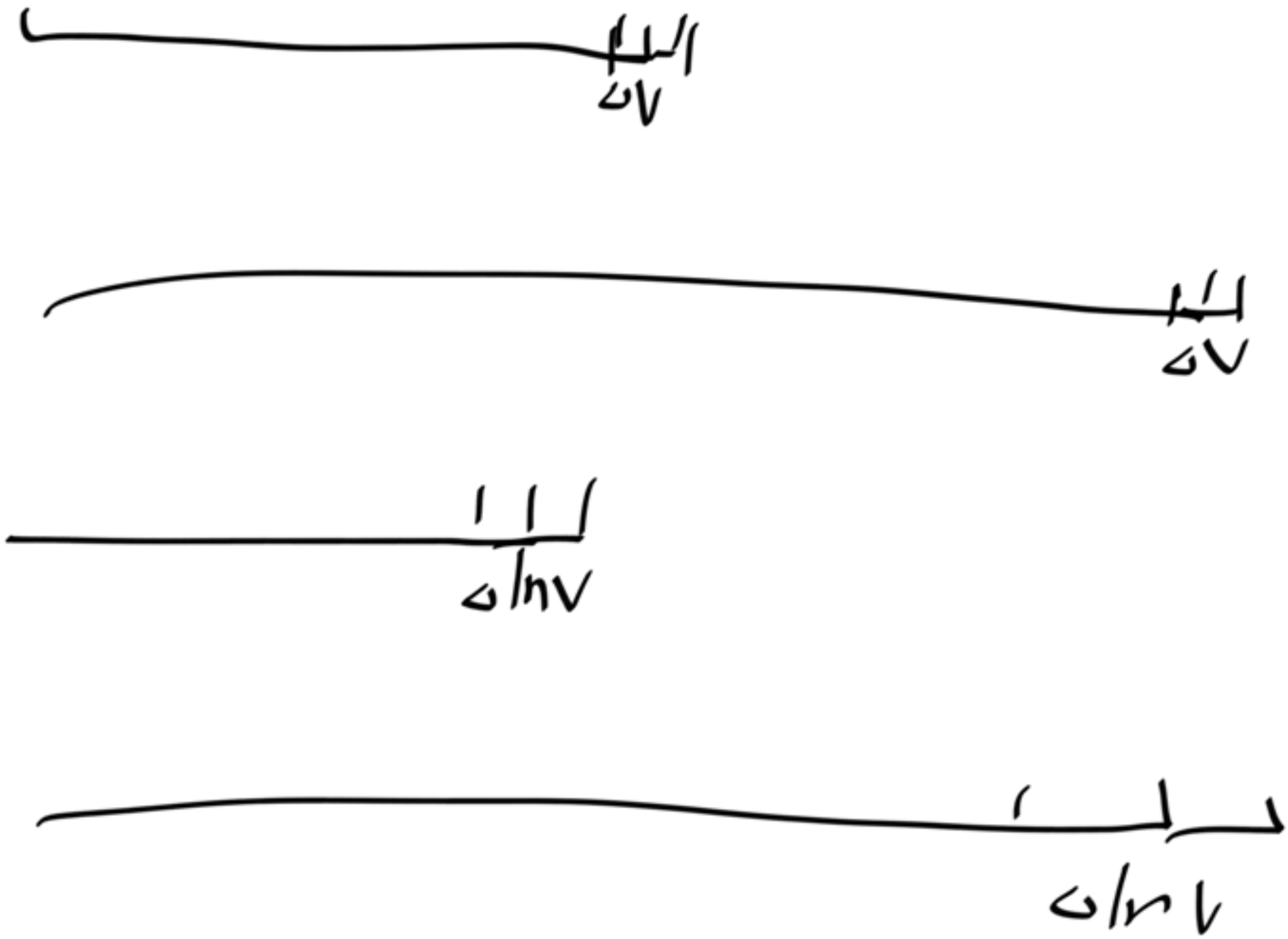
$$d\left(e^{-\beta A} e^{-\beta PV}\right)$$

$$= e^{-\beta A} e^{-\beta PV} (-\beta P)\, dV$$

$$+ \underline{e^{-\beta PV} \cdot \left(\frac{\partial e^{-\beta A}}{\partial V}\right)_{NT} \cdot dV}$$

$$\langle P_V \rangle = \frac{P}{\Delta}\left[\overbrace{\int_{\underbrace{lb(V\to 0)}_{0}}^{ub(V\to\infty)} d\left(e^{-\beta PV} e^{-\beta A}\right)}^{=0} - \int_0^{+\infty} (-\beta P)\, e^{-\beta A} e^{-\beta PV}\, dV \right]$$

$$= \frac{p}{\Delta} \underbrace{\int_0^{+\infty} e^{-\beta A} e^{-\beta p V} \cdot dV}_{\Delta} = p$$



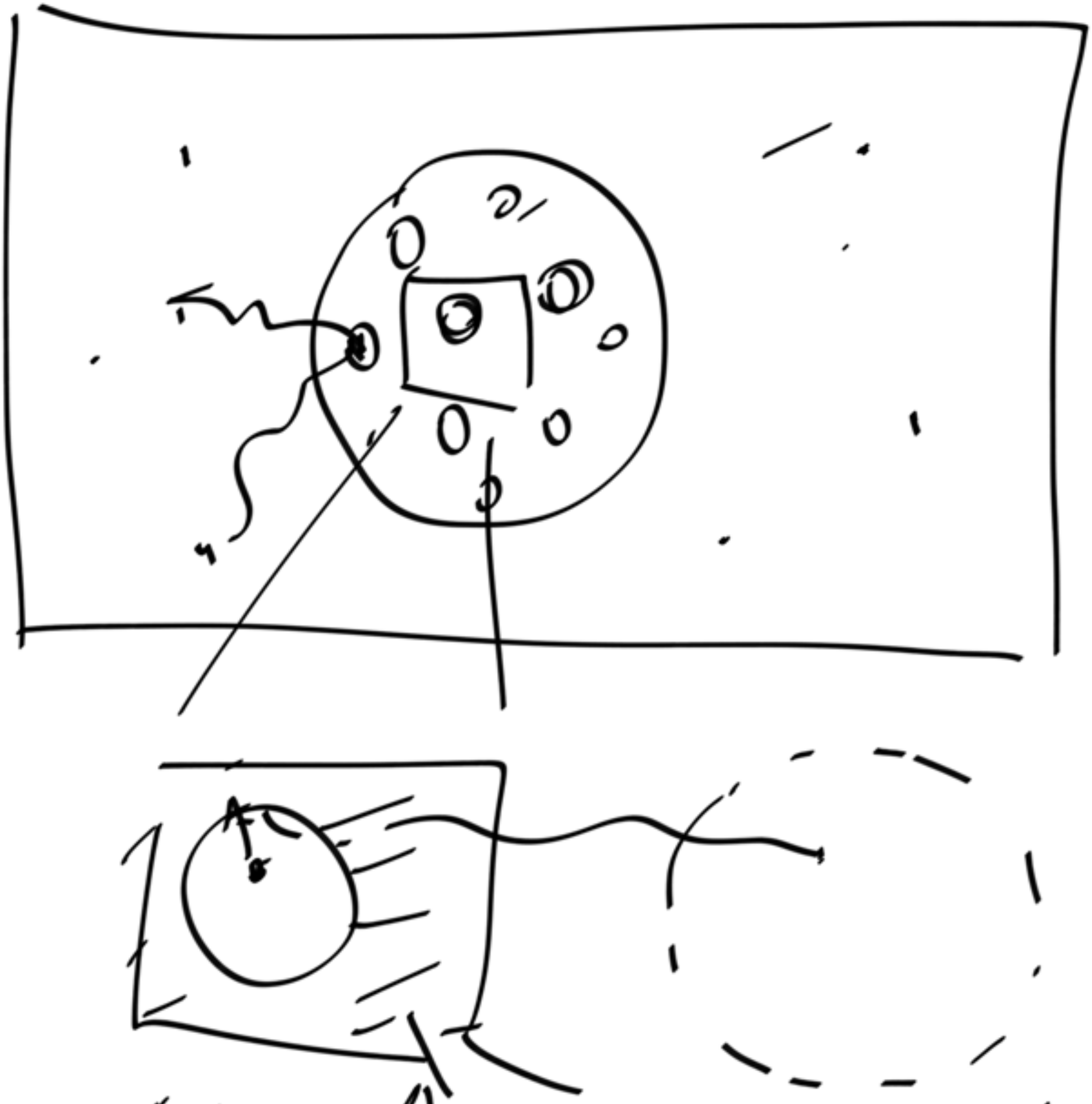
$$P(V) \cancel{\propto} V^{N} \cdot e^{-\beta PV} e^{-\beta U(\vec{S_N}, L(V))}$$

$$\Delta \cancel{\propto} \int \underline{dV}\, V^{N} e^{-\beta PV} e^{-\beta U(\vec{S_N})}$$

$$\int dV\, V^{-1} V^{N+1} e^{-\beta PV} \cdot e^{-\beta U}$$

$$\int d\ln V\, V^{N+1} e^{-\beta PV} e^{-\beta U}$$

$$P'(V) \propto V^{N+1} e^{-\beta PV} e^{-\beta U}$$



NW $+1$ if $\rightarrow$ cavity

-1 cavity $\rightarrow$ i.g.

e.g $\rightarrow \mu_{cav} = \mu_{i.g.}$

$$\mu = \left(\frac{\partial A}{\partial N}\right)_{V,T}$$

$$= A(N+1) - A(N)$$

$$= -\frac{1}{\beta} \ln \frac{Q(N+1)}{Q(N)}$$

$$Q(N) = \frac{1}{\Lambda^{3N} N!} \underbrace{\int e^{-\beta U(\vec{q}_N)} \, d\vec{q}_N}$$

$$\underline{\underline{Q(N)_{i.g.}}} = \frac{V^N}{\Lambda^{3N} N!}$$

$$\mu_{ig} = -\frac{1}{\beta}\ln\frac{V}{\Lambda^3(N+1)}$$

$$= -\frac{1}{\beta}\ln\frac{1}{\Lambda^3} - \frac{1}{\beta}\ln\frac{V}{N+1}$$

$$\frac{N+1}{V} \sim \rho$$

$$= -\frac{1}{\beta}\ln\frac{1}{\Lambda^3} + \frac{1}{\beta}\ln\rho$$

$$\Xi = \sum_{N=0}^{\infty} \underline{e^{\beta\mu N}}\ \underline{Q(N,V,T)}$$

$$\underline{P(N) = \frac{e^{\beta\mu N} Q(N,V,T)}{\Xi}}$$

$$\begin{cases} N \longrightarrow N+1 & \text{(insertion)} \\ N \longrightarrow N-1 & \text{(deletion)} \end{cases}$$

$$P(N) \cdot \underline{\alpha(N \to N+1)} \cdot acc(N \to N+1) =$$

$$P(N+1)\, \overline{\alpha(N+1 \to N)} \cdot acc(N+1 \to N)$$

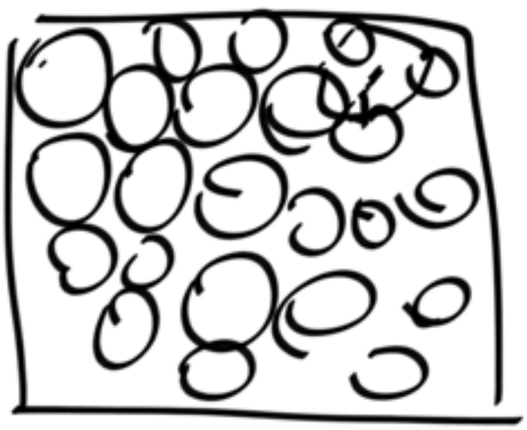
$$\frac{acc(N \to N+1)}{acc(N+1 \to N)} = \frac{P(N+1)}{P(N)}$$

$$= \frac{e^{\beta\mu} V}{\Lambda^3 (N+1)} e^{-\beta[U(S_{N+1}) - U(S_N)]}$$

$$\frac{acc(N \to N+1)}{acc(N-1 \to N)} = \frac{P(N-1)}{P(N)}$$

$$= \frac{\Lambda^3 N}{V e^{\beta\mu}} e^{-\beta[U(N-1) - U(N)]}$$

$$acc(N, N+1) = \min\left[1, \frac{V e^{\beta\mu}}{\Lambda^3 (N+1)} e^{-\beta(U(s_{N+1}) - U(s_N))}\right]$$

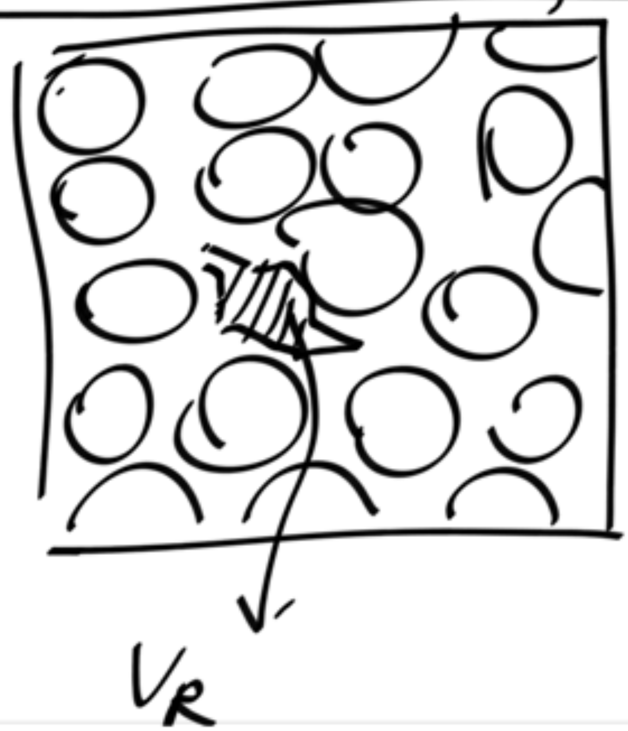


Biased MC:

$$\pi(\vec{o} \to \vec{n}) = \alpha(\vec{o} \to \vec{n}) \cdot acc(\vec{o} \to \vec{n})$$

$$\frac{acc(\vec{o} \to \vec{n})}{acc(\vec{n} \to \vec{o})} = \frac{\alpha(\vec{n} \to \vec{o})}{\alpha(\vec{o} \to \vec{n})} \cdot e^{-\beta[U(\vec{n}) - U(\vec{o})]}$$

$$= \frac{f(U(\vec{o}))}{f(U(\vec{n}))} e^{-\beta[U(\vec{n}) - U(\vec{o})]}$$



$$\frac{acc(N \to N+1)}{acc(N+1 \to N)}$$

$$= \frac{\alpha(N+1 \to N)}{\alpha(N \to N+1)} \cdot e^{-\beta[U(N+1) - U(N)]} \frac{e^{\beta\mu} V}{\Lambda^3 (N+1)}$$

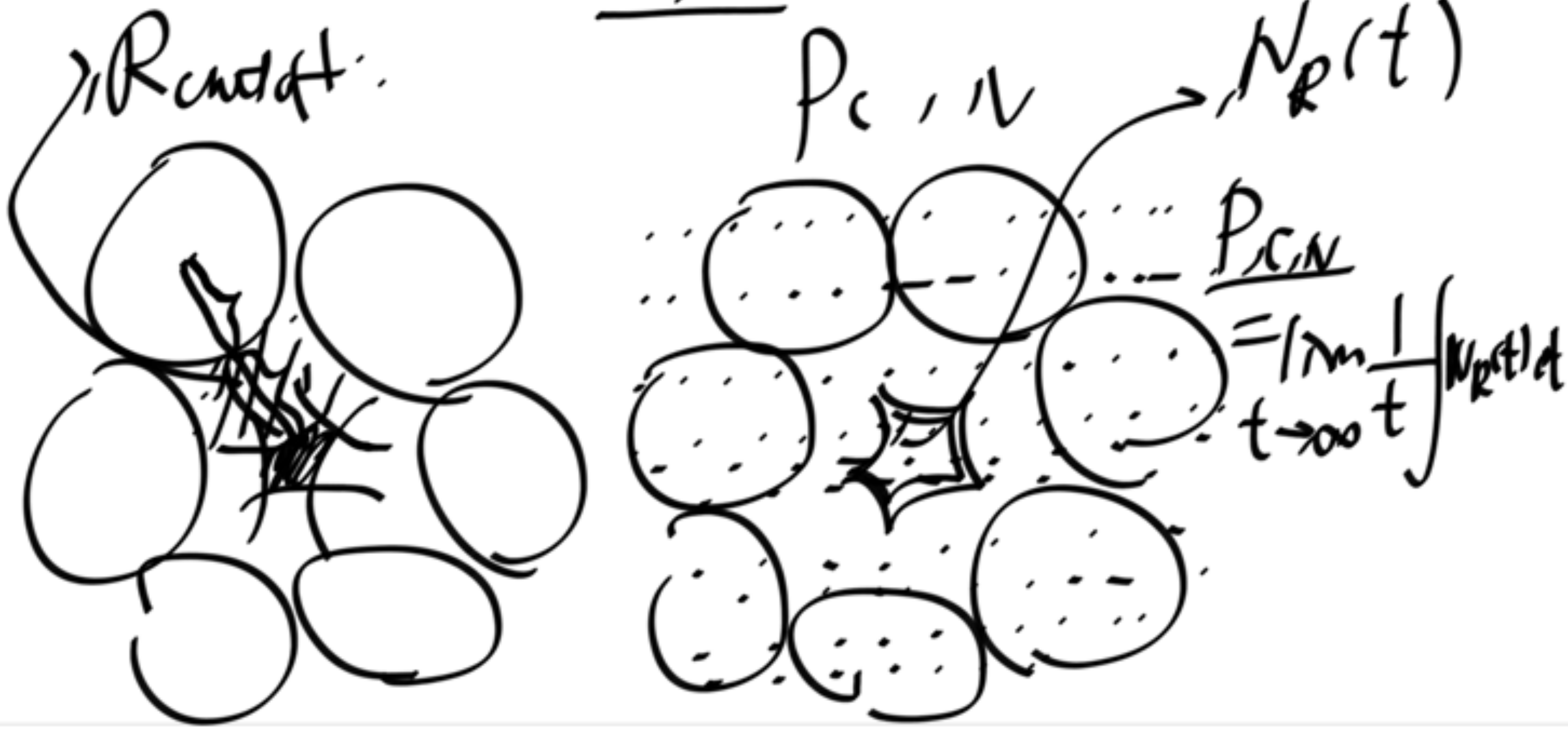
$$\alpha(N+1 \to N) \propto \frac{1}{V}$$

$$\alpha(N \to N+1) \propto \frac{1}{V}$$

$$\alpha'(N \to N+1) \propto \frac{1}{V_R}$$

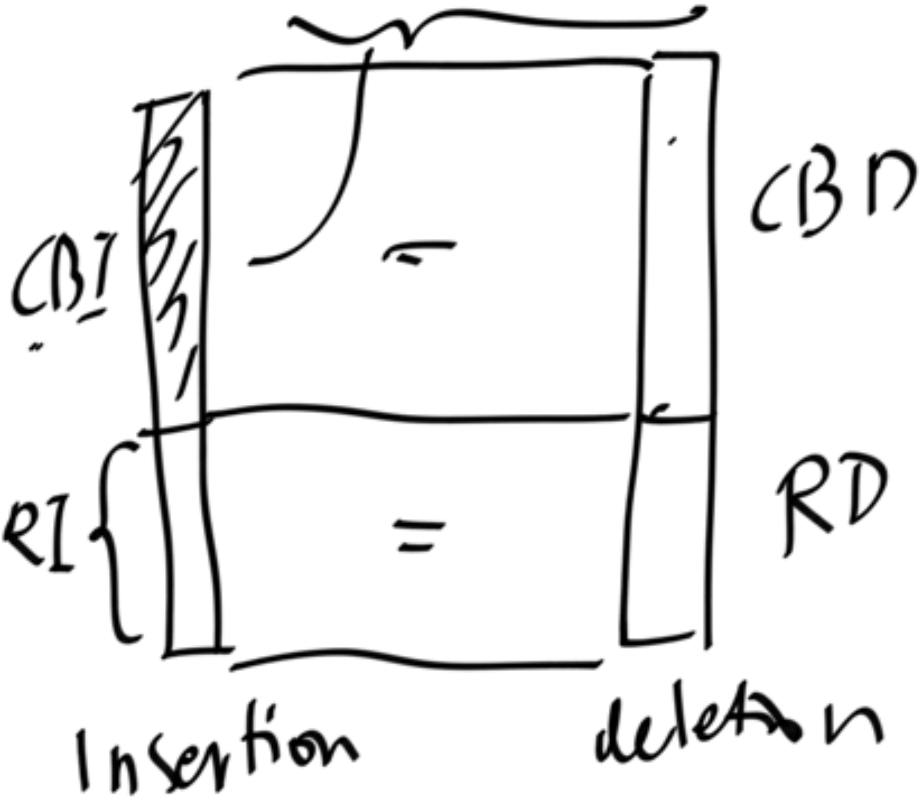
$$\frac{acc(N \to N+1)}{acc(N+1 \to N)} = \frac{V_R}{V} \frac{e^{\beta\mu} V}{\Lambda^3 (N+1)} e^{-\beta(U(N+1) - U(N))}$$

$P_{C,N}$



$P(i,N)$ $\quad$ N_{tot}

$$\begin{cases} (1-P(i,N))^{N_{tot}} \longrightarrow RI \\ 1-(1-P(i,N))^{N_{tot}} \longrightarrow CBI \end{cases}$$



RI:

$$\frac{acc(N \to N+1)}{acc(N+1 \to N)} = \frac{\frac{\alpha_R(N+1 \to N)}{\alpha_R(N \to N+1)}}{(1-P_{c,N})^{N+1}} \cdot \frac{e^{\beta\mu} V\, e^{-\beta(\ldots)}}{\Lambda^3 N+1\; e^{\bar{U}_N}}$$

$$\underline{\alpha_R(N+1, N) = (1-P_{c,N})^{N+1}}$$

$$\left(\frac{acc(N \to N+1)}{acc(N+1 \to N)} = \frac{e^{\beta\mu} V}{\Lambda^3 (N+1)} e^{-\beta \cdots}\right.$$

CBI:

$$\frac{acc'(N \to N+1)}{acc'(N+1 \to N)} = \frac{\alpha_{CB}(N+1 \to N)}{1-(1-p_{c,n})^{N_{tot}}} \cdot$$

$$\underline{p_{c,N}} \cdot \frac{V}{\Lambda^3(N+1)} e^{-\beta \cdots}$$

$$\alpha_{CB}(N+1 \to N) = 1-(1-p_{c,n})^{N_{tot}}$$

$$\frac{acc'(N \to N+1)}{acc'(N+1 \to N)} = \underline{\underline{p_{c,N}}} \frac{V e^{\beta\mu}}{\Lambda^3(N+1)} e^{-\beta \cdots}$$

$$\frac{acc(N+1 \to N)}{acc(N \to N+1)} = \frac{\Lambda^3(N+1)}{p_{c,N} V e^{+\beta\mu}} e^{-\beta(U(N-1)-U(N))}$$

$$\frac{acc(N \to N-1)}{acc(N-1 \to N)} = \frac{\Lambda^3 N}{p_{c,N-1} V e^{\beta\mu}} e^{-\beta(U(N-1)-U(N))}$$

Algorithm:

① Initiate N, $\tilde{S}_n$

② particle movement at NVT

③ if Rand < 0.5:

Insertion:

generate N tol print

Calculate N_R

Update $P_{c,N}$

If $N_R = 0$:

Random Insertion:

$$acc = \frac{V e^{\beta\mu}}{\Lambda^3 (N+1)} e^{-\beta \cdots}$$

else:

CBI:

$$acc = P_{c,N} \cdot \frac{V e^{\beta\mu}}{\Lambda^3 (N+1)} e^{-\beta \cdots}$$

else:

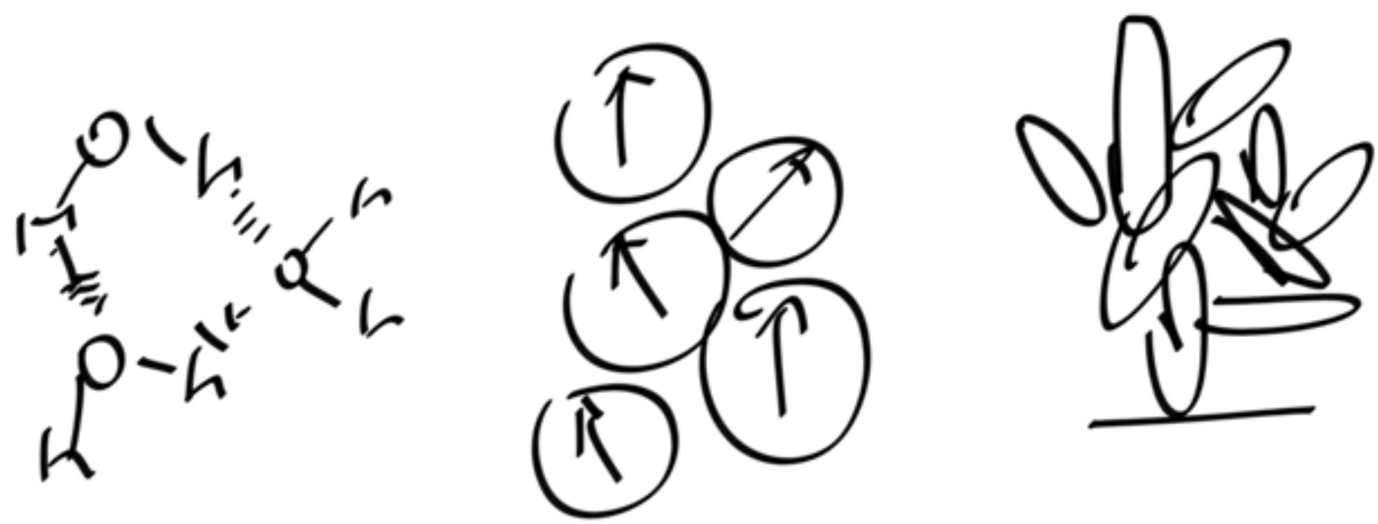
if $Rand < (1 - P_{c,N})^{N_{tot}}$:

RD: $$acc = \frac{\Lambda^3 N}{V e^{\beta\mu}} e^{-\beta(U(N-1) - U(N))}$$

else:

CBD: $$acc = \frac{\Lambda^3 N}{P_{c,N} V_1 e^{\beta\mu}} e^{-\beta(U(N-1) - U(N))}$$

Orientational Bias:



$$\mathcal{U}(S_1) = \mathcal{U}_{pos} + \mathcal{U}_{ort}$$

$$\mathcal{U}_{pos}(S_0) + \Big(\underbrace{\mathcal{U}(\vec{b})}_{\mathcal{U}_{ort}} \Big)$$

① : randomly displace $\vec{n}$, $\mathcal{U}_{pos}(\vec{n})$

② : randomly generate k oriation

$\{\vec{b}_1, \vec{b}_2 \cdots \vec{b}_k\}$, $\mathcal{U}_{ort}(\vec{b}_i)$

③ : Rosenbluth factor : $\omega(\vec{n}) = \sum_i^k e^{-\beta \mathcal{U}_{ort}(\vec{b}_i)}$

select an ort $\vec{b}_n$: $P(\vec{b}_n) = \dfrac{e^{-\beta \mathcal{U}_{ort}(\vec{b}_n)}}{\omega(\vec{n})}$

④ $\vec{o}$, calculate $U_{pos}(\vec{o})$, $U_{ort}(\vec{b_o})$

randomly generate $k-1$,

$$\{\vec{b_2}', \vec{b_3}', \ldots \vec{b_k}'\}$$

calculate Rosenbluth factor:

$$w(\vec{o}) = e^{-\beta U_{ort}(\vec{b_o})} + \sum_{i=2}^{k} e^{-\beta U_{ort}(\vec{b_i}')}$$

⑤ $acc(\vec{o} \to \vec{n})$

$$= \min\left(1, \frac{w(\vec{n})}{w(\vec{o})} e^{-\beta(U_{pos}(\vec{n}) - U_{pos}(\vec{o}))}\right)$$

$$\{\vec{b}\}_k = \{\vec{b_1}, \vec{b_2}, \cdots \vec{b_k}\}$$

$$\underline{B_n} = \{ \{\vec{b}\}_k \mid \vec{b_n} \in \{\vec{b}\}_k \} \to \{\vec{b_n}, \underbrace{\vec{b^*}}_{k-1}\}$$

$$\underline{B_o} = \{ (\vec{b})_k \mid \vec{b_o} \in \{\vec{b}\}_k \} \to \{\vec{b_o}, \underbrace{\vec{b^*}}_{k-1}\}$$

$$\underline{P(\vec{o})} \cdot \underbrace{\pi(\vec{o} \to \vec{n})} = P(\vec{n}) \cdot \pi(\vec{n} \to \vec{o})$$

$$\frac{1}{n}\sum_j \alpha(\vec{b_o}, \vec{b^*} \to \vec{b_n}, \vec{b^*}) \cdot \underline{acc(\vec{o} \to \vec{n})}$$

$acc(\vec{o} \to \vec{n}) \times$

$$\frac{1}{n}\sum_i^{i}\sum_j^{j} \alpha(\vec{b_{o_i}}, \vec{b^*_i} \to \vec{b_n}, b_{j^*})$$

$\bar{\pi}(\vec{n} \to \vec{o})$

$$= \frac{1}{n} \sum_i \sum_j \alpha\left(\begin{matrix}\vec{b_n} \\ b_i^*\end{matrix} \to \begin{matrix}\vec{b_o} \\ b_j^*\end{matrix}\right)$$

$acc(\vec{n} \to \vec{o})$

$\forall i, j$

$$p(\vec{o}) \cdot acc(\vec{o} \to \vec{n}) \cdot \alpha\left(\begin{matrix}\vec{b_o} \\ b_i^*\end{matrix} - \begin{matrix}\vec{b_n} \\ b_j^*\end{matrix}\right)$$

$$= p(\vec{n})\, acc(\vec{n} \to \vec{o}) \cdot \alpha\left(\begin{matrix}\vec{b_n} \\ b_i^*\end{matrix} \to \begin{matrix}\vec{b_o} \\ b_j^*\end{matrix}\right)$$

$$\frac{acc(\vec{o} \to \vec{n})}{acc(\vec{n} \to \vec{o})} = \underbrace{\frac{\alpha\left(\begin{matrix}\vec{b_n} \\ b^*\end{matrix} \to \begin{matrix}\vec{b_o} \\ b^*\end{matrix}\right)}{\alpha\left(\begin{matrix}\vec{b_o} \\ b^*\end{matrix} \to \begin{matrix}\vec{b_n} \\ b^*\end{matrix}\right)} \; \frac{e^{-\beta(U(\vec{n}) - U(\vec{o}))}}{}}$$

$$\frac{e^{-\beta U_{out}(\vec{o})}}{w(\vec{o})} \qquad \frac{e^{-\beta U_{out}(\vec{b_n})}}{w(\vec{n})}$$

$$\frac{acc(\vec{o}\to\vec{n})}{acc(\vec{n}\to\vec{o})} = \frac{w(\vec{n})}{w(\vec{o})} \frac{e^{\beta U_{ort}(\vec{b}_o)}}{e^{-\beta U_{ort}(\vec{b}_n)}} e^{-\beta(U(\vec{n}) - U(\vec{o}))}$$

$$U(\vec{n}) = U_{pos}(\vec{n}) + U_{ort}(\vec{b}_n)$$

$$U(\vec{o}) = U_{pos}(\vec{o}) + U_{ort}(\vec{b}_o)$$

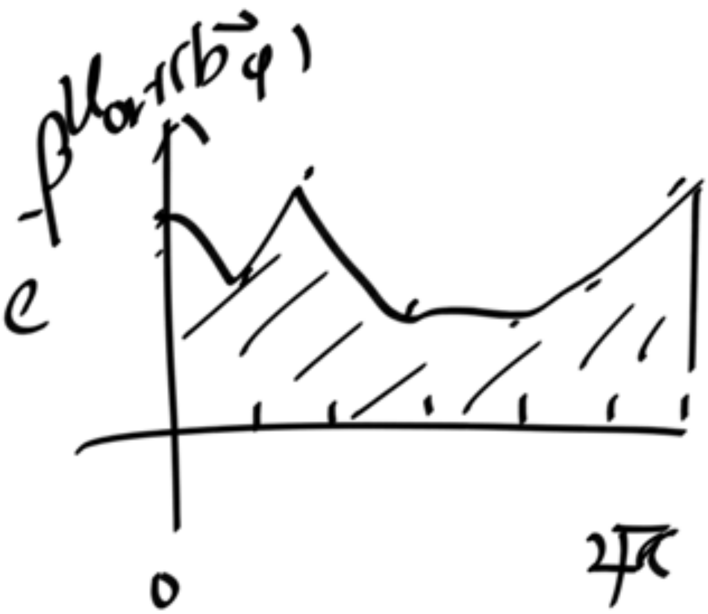
$$= \frac{w(\vec{n})}{w(\vec{o})} e^{-\beta[U_{pos}(\vec{n}) - U_{pos}(\vec{o})]}$$

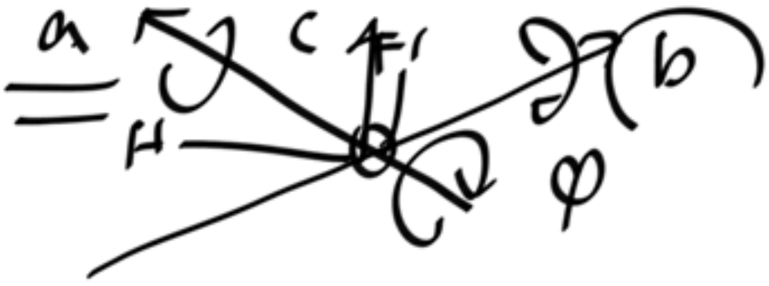
Insertion a water molecule

$$\frac{acc(N\to N+1)}{acc(N+1\to N)} = \frac{\alpha(N+1\to N)}{\alpha(N\to N+1)} \frac{P(N+1)}{P(N)}$$

$$= \boxed{\frac{w(N+1)}{w(N)}} \frac{e^{\beta\mu}V}{\Lambda^3(N+1)} e^{-\beta[U(N+1) - U(N)]}$$

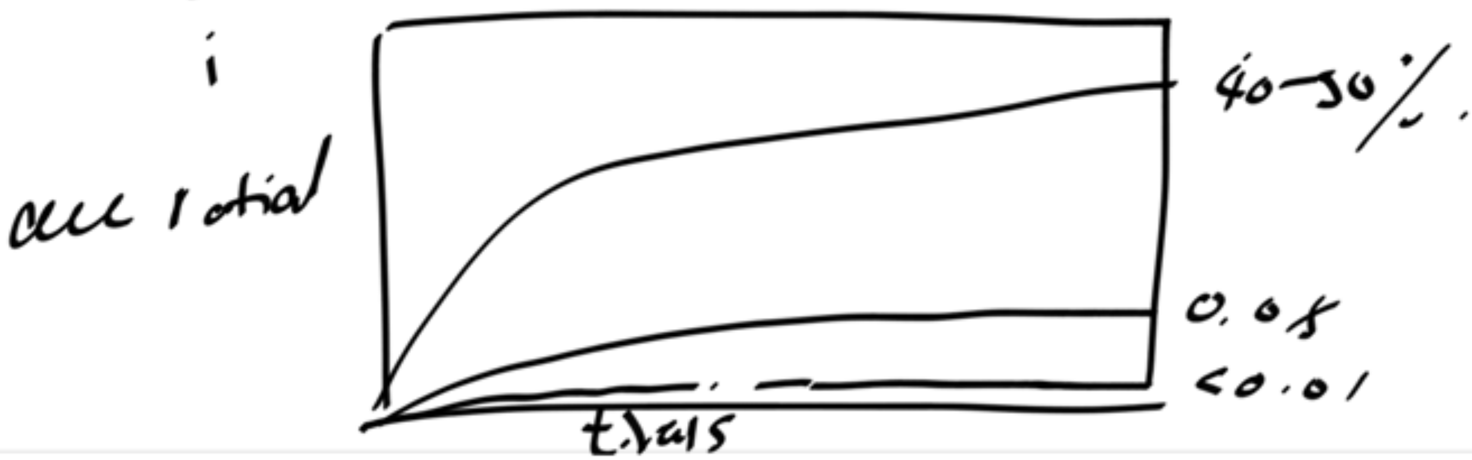
$$= \frac{1}{f(\vec{S}_n, \vec{w}_n)}$$





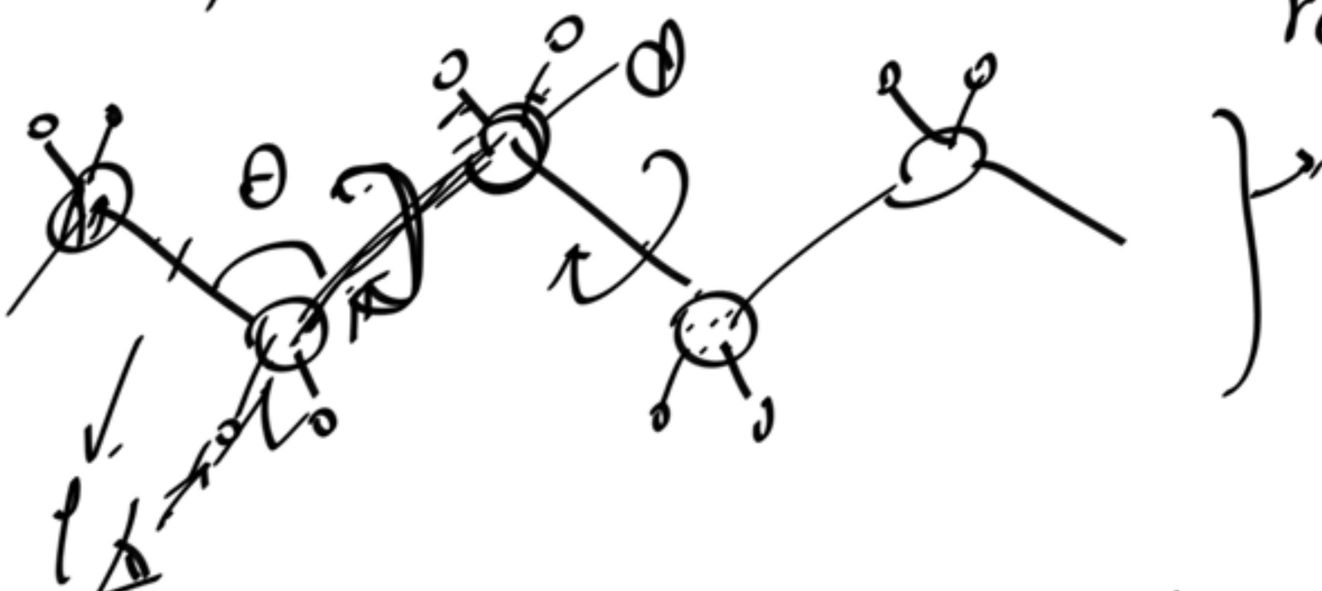
$$f(\vec{s_n}, \vec{b_\varphi}) = \frac{e^{-\beta U_{ort}(\vec{b_\varphi})}}{\sum_i e^{-\beta U_{ort}(\vec{b_i})}}$$

$$acc = \frac{1}{\sum_i e^{-\beta U_{ort}}} \frac{V e^{\beta\mu}}{\Lambda^3 (N+1)} \cdot e^{-\beta\left(U_{pol}(N+1) - U_{pol}(N)\right)}$$



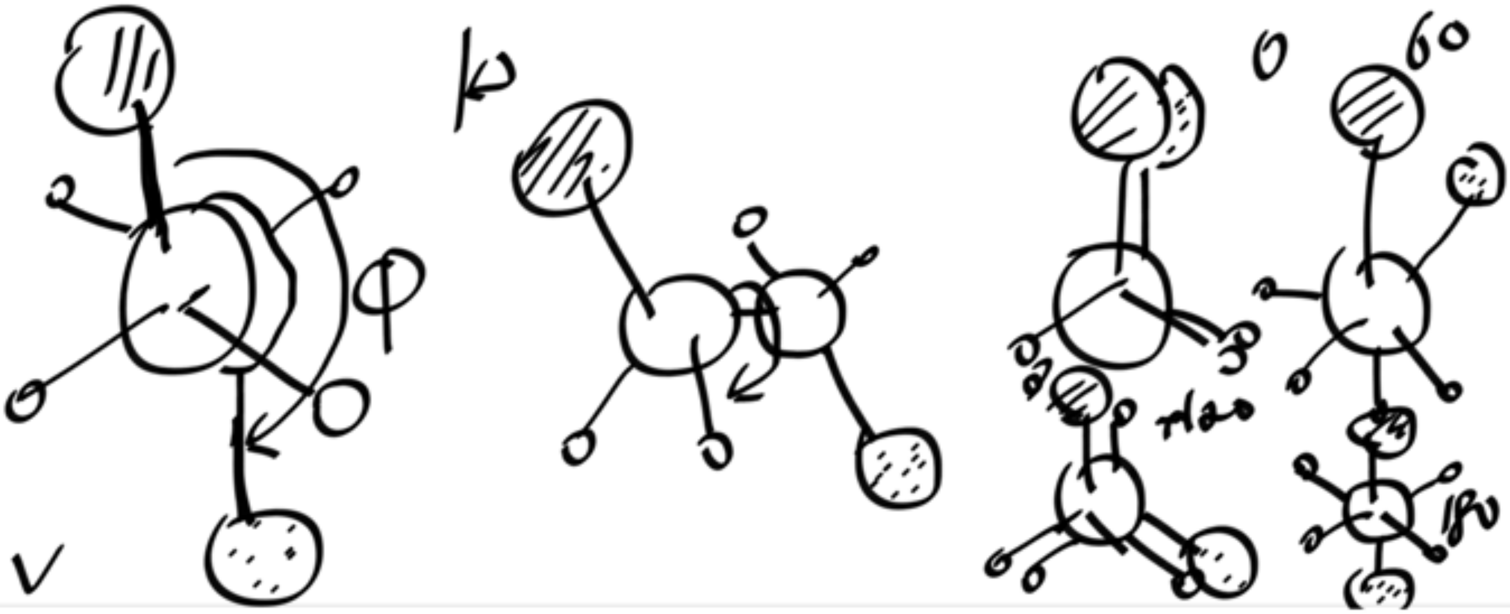
MC of Polymers:

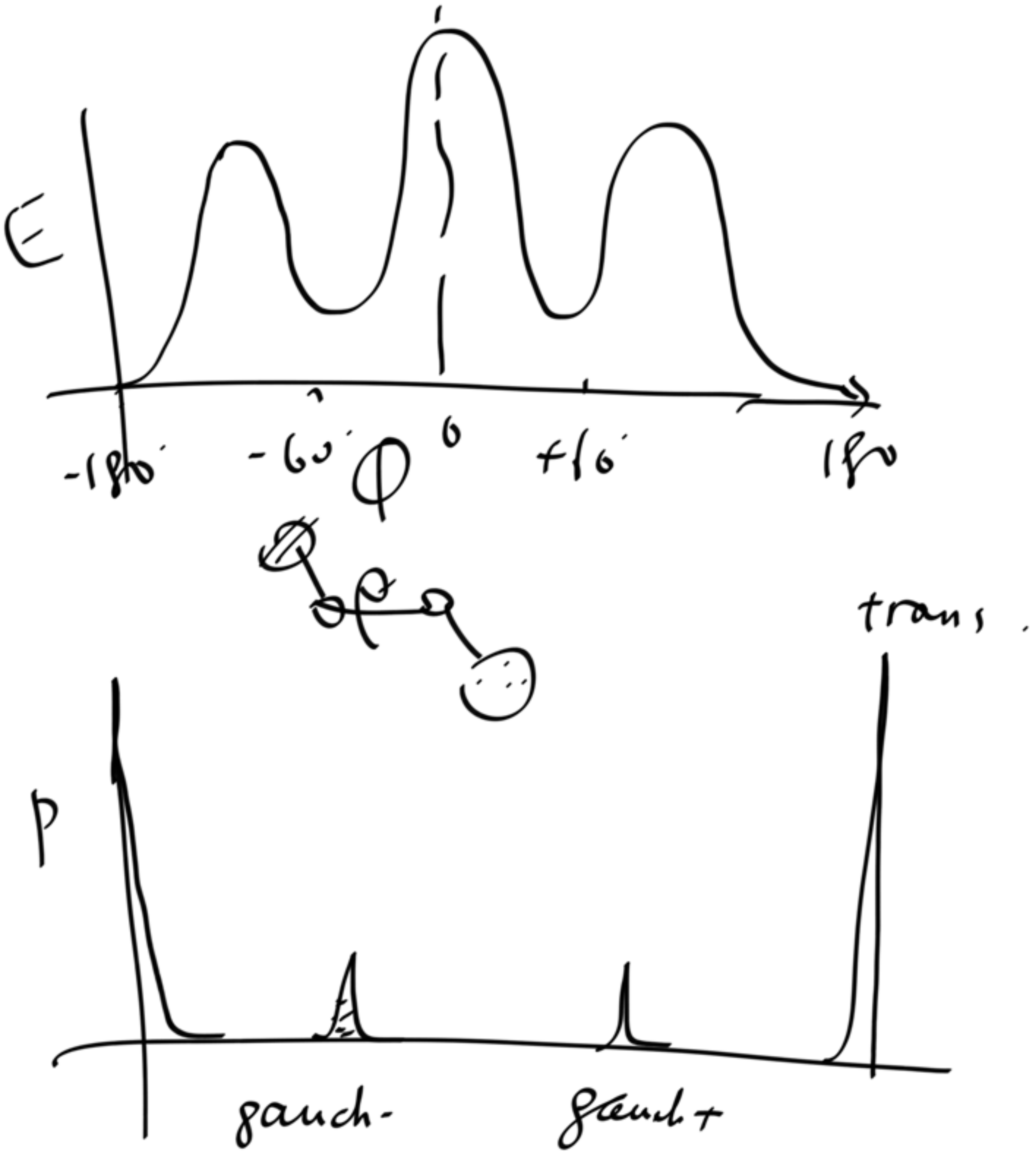
polyethylene $-(CH_2)_n-$



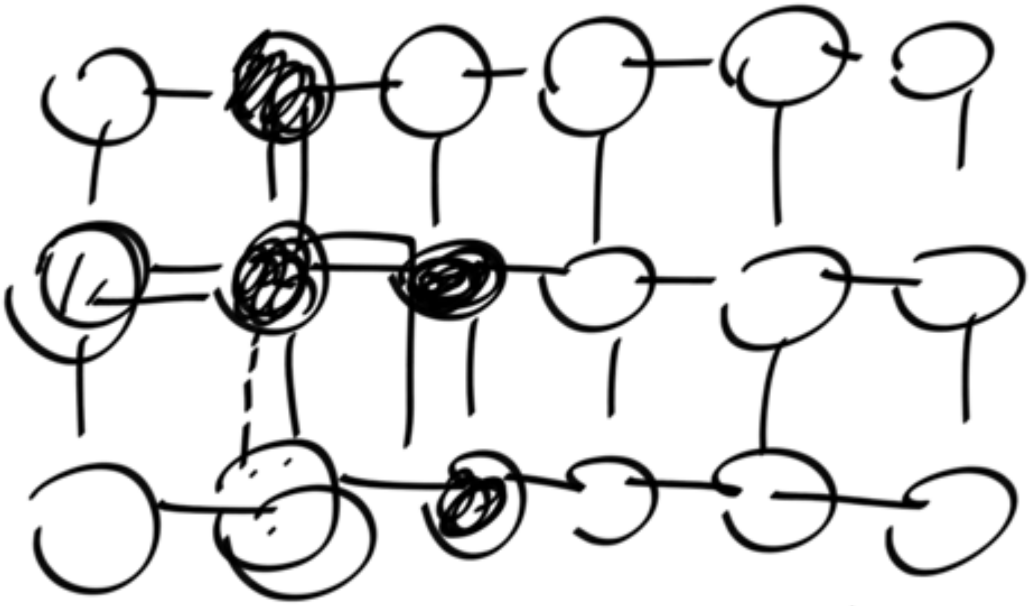
realistic

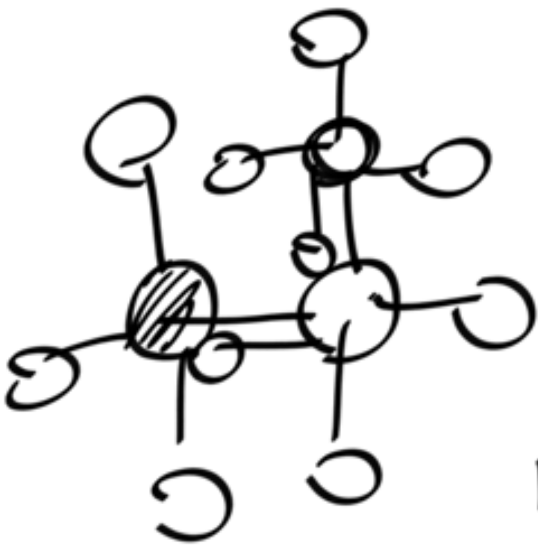
radius of gyration; end-to-end distance.




E
-180
-60
Φ
0
+60
180
trans
P
gauch-
gauch+

lattice:





① random-walk (RW)

$N : Z \propto 4^N$

$\underline{q}^N$

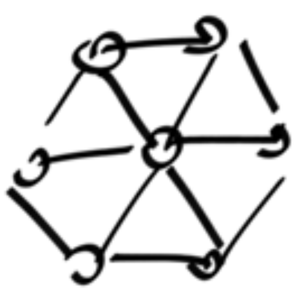
square lattice

$\underline{q} = 4$

$\underline{q} = 6$

hexagonal lattice

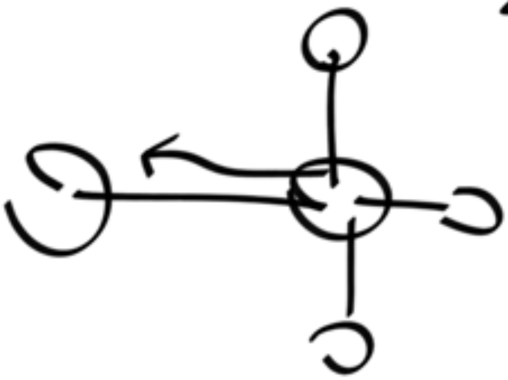
$\underline{q} = 6$



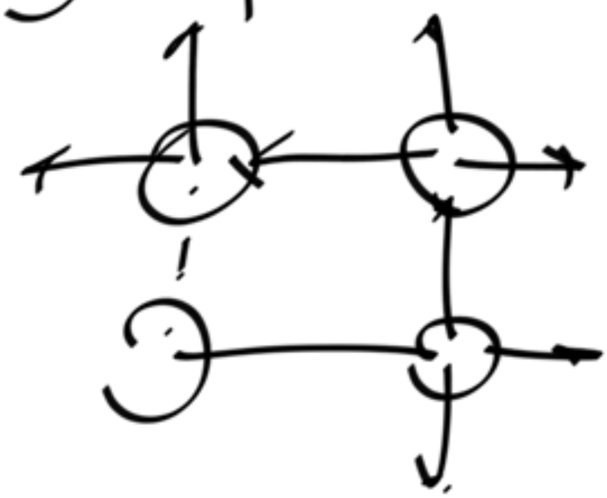
② NRRW

non-reversible

$$Z \propto (\underline{q} - 1)^N$$

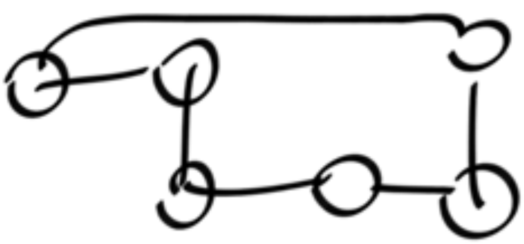


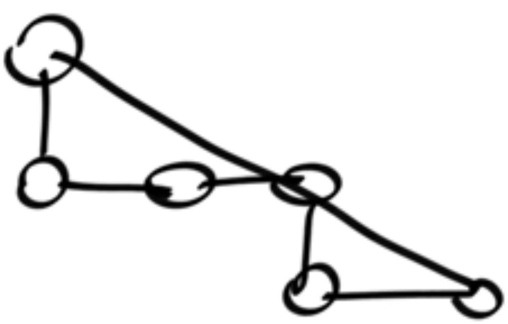
③ self-avoidance walk:



$$Z \propto N^{\gamma} \, \underline{\underline{q}}_{eff}^{\,N}$$

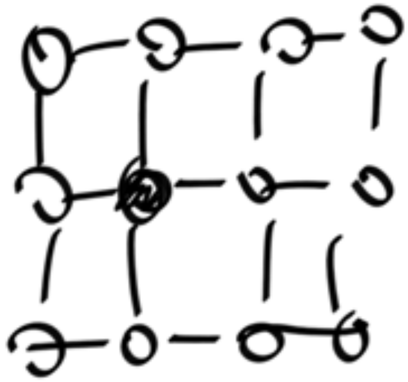
$$\underline{q}_{eff} < \underline{q} - 1$$



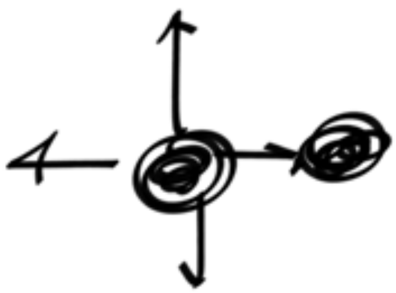


Simple Sampling of SAW

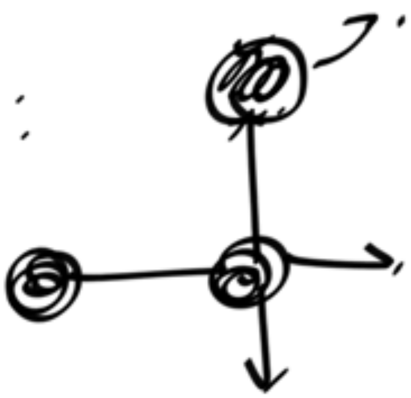
① choose a random site



② choose a random direction.



③ i:



no clash

there is clash
save this conf
as a conf for
polymer $\leq i$

④ until $i = N$
→ save this conf as polymer $= N$

$$P(n, \eta_1, \eta_2, \cdots \eta_{N-1}] \rightarrow \underline{\underline{SAW}}$$

$$= P(n', \Pi_1', \eta_2', \eta_{N}')$$

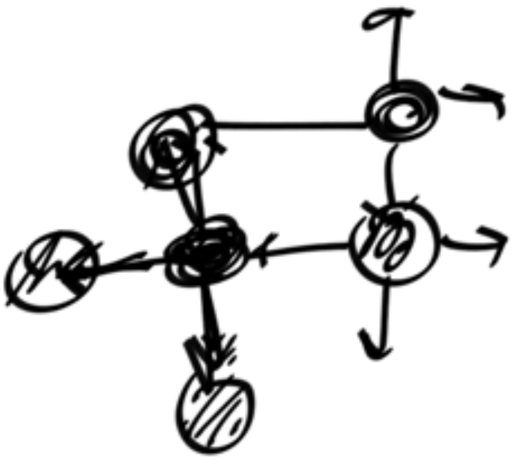
$$Z = (\underline{q}-1)^N$$

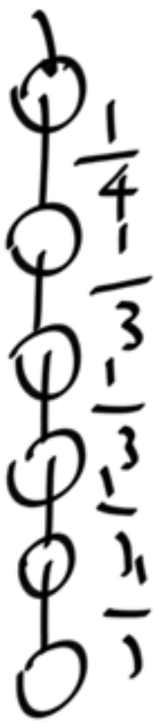
$$Z_{SAW} = N^{\gamma} q_{eff}^{N} \rightarrow \text{Attribution problem.}$$

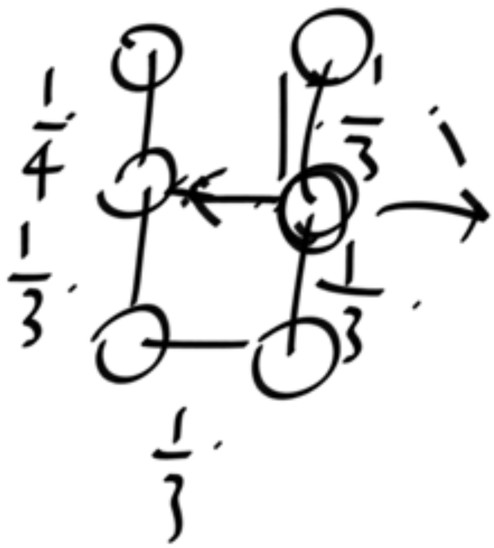
$$\frac{Z_{SAW}}{Z} = N^{\gamma} \cdot \left(\frac{q_{eff}}{\underline{q}-1}\right)^{N} \rightsquigarrow \overset{N_1}{\underline{\underline{30}}}$$

$$q_{eff} < \underline{q} - 1$$

current lim. t.







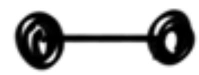
simple sampling: $\frac{1}{4}\times\left(\frac{1}{3}\right)^4$ $\quad \frac{1}{4}\times\left(\frac{1}{3}\right)^4$

biased sampling: $\frac{1}{4}\times\left(\frac{1}{3}\right)^4$ $\quad \frac{1}{4}\times\left(\frac{1}{3}\right)^3\times\frac{1}{2}$. →

Rosenbluth Sampling

① start at a random lattice point:

② $i=1$, $P_r^b = \frac{1}{q} = \frac{1}{k_1}$



③ $i>1$, $P_r^b = \frac{1}{k_i}$ $\quad 0<k_i \le q-1$

④ if $k_i=0$, start over

⑤ $i=N$. P_r

generate a factor associated with this conf.

accept $(\vec{r}_0, \vec{r}_1, \vec{r}_2, \ldots \vec{r}_{N-1})$, $W(\vec{n}) = \prod_{i=1}^{N} \left(\frac{k_i}{q-1}\right)$

$$\langle A \rangle = \frac{\sum_{j=1}^{n} W(\vec{r}_j) \cdot A(\vec{r}_j)}{\sum W(\vec{r}_j)}$$

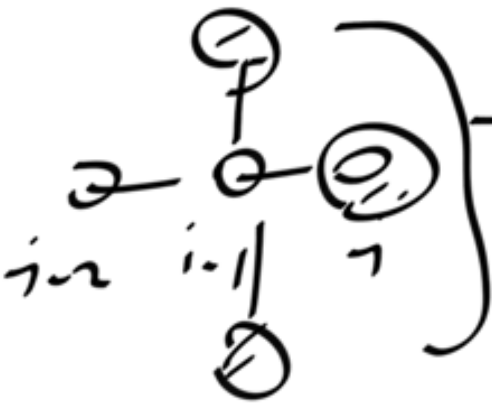
NRRW

$$\langle A \rangle = \frac{\sum_{j=1}^{n} A(\vec{r}_j)}{n}$$

General algorithm of Rosenbluth Sampling

① select one unit and place it at a random site., $\mathcal{U}(\vec{o})$, $w_1 = e^{-\beta \mathcal{U}(\vec{o})}$

② $i: 2, 3, \cdots \ell$, consider $\underline{g}$ direction from segment $i-1$, for each direction (j), $\underline{u^{(i)}(j)}$



$\rightarrow g = 3$

$$p^{(i)}(n_i) = \frac{e^{-\beta u^{(i)}(n_i)}}{\underline{\underline{W_i}}}$$

$$W_i = \sum_{j=1}^{g} e^{-\beta u^{(i)}(j)}$$

$u^{(i)}(j)$

$$\boxed{U(\vec{r}_\ell) = \sum_{i=1}^{\ell} u^{(i)}(n_i)}$$

③ until entire molecule grows.

$$W^{RS}(\vec{n}) = \prod_{i=1}^{\ell} \frac{W_i}{g}$$

$$\prod_{i=1}^{\ell} \frac{e^{-\beta u^{(i)}(n_i)}}{\omega_i} \cdot W(\vec{n}) \longrightarrow e^{-\beta U(\vec{n})} \cdot P(\vec{n})$$

$$W(\vec{n}) = \prod_i \frac{\omega_i}{e^{-\beta u^{(i)}(n_i)}} \, e^{-\beta u(\vec{n})} \cdot \left(\frac{1}{g}\right)^{\ell}$$

$$= \prod_i \frac{\omega_i}{g} \cdot \frac{e^{-\beta u(\vec{n})}}{e^{-\beta \sum_i u^{(i)}(n_i)}}$$

$$= \prod_i \frac{\omega_i}{g}$$

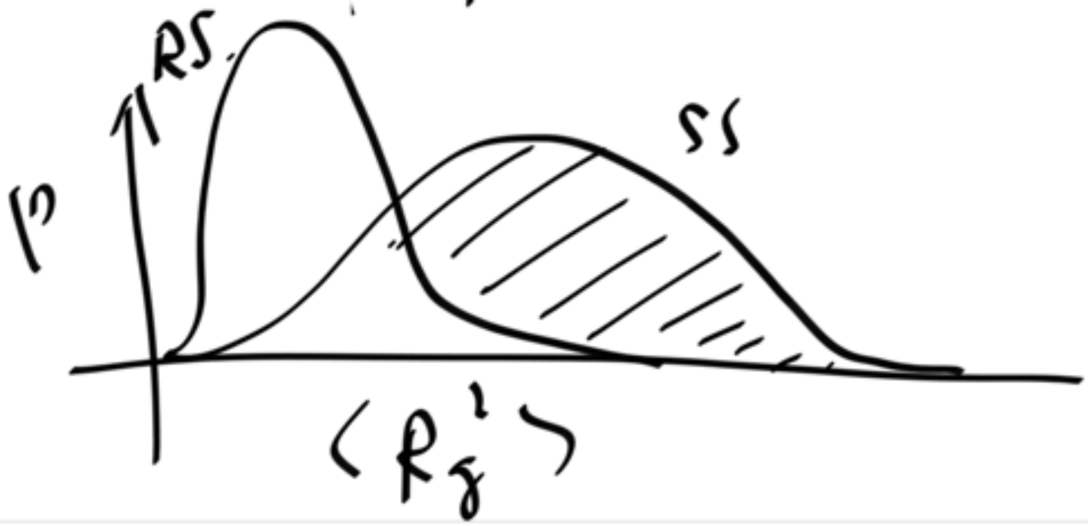
$$\langle A \rangle = \frac{\sum_{i=1}^{n} A(\vec{r}_i) \cdot W^{RS}(\vec{r}_i)}{\sum_{i=1}^{n} W^{RS}(\vec{r}_i)}$$

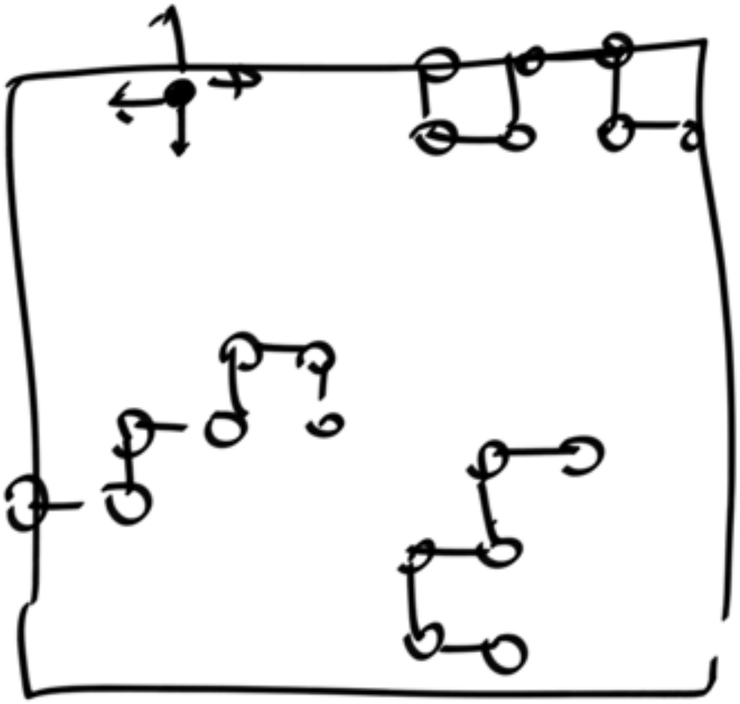
RS: prefer compact structures:

$$P_r^{SS}(\vec{n}) = \text{const} \propto \left(\frac{1}{q}\right)^n$$

$$P_r^{RS} \propto \prod_i \frac{1}{k_i}$$

$n \sim 100$





① first randomly choose first unit of a chain at a random position.

$$u_1(n), \quad w_1(n) = \underline{\underline{k}}\, e^{-\beta u_1(n)}$$

② $i > 1$, sample k direction for $j = 1, \ldots, k$, $u^{(i)}(j)$

$$p^{(i)}(n_i) = \frac{e^{-\beta u^{(i)}(n_i)}}{\underbrace{\sum_{j=1}^{k} e^{-\beta u^{(i)}(j)}}_{\to\, w_i(n)}}$$

③ when entire (ℓ) grows;

$$W(\vec{n}) = \prod_{i=1}^{\ell} w_i(n)$$

④ random choose one of old chains: retrace the old chains $(\vec{o})$,

$$W(\vec{o}) = \prod_{i=1}^{\ell} w_i(o)$$

⑤ $\vec{o} \to \vec{n}$,

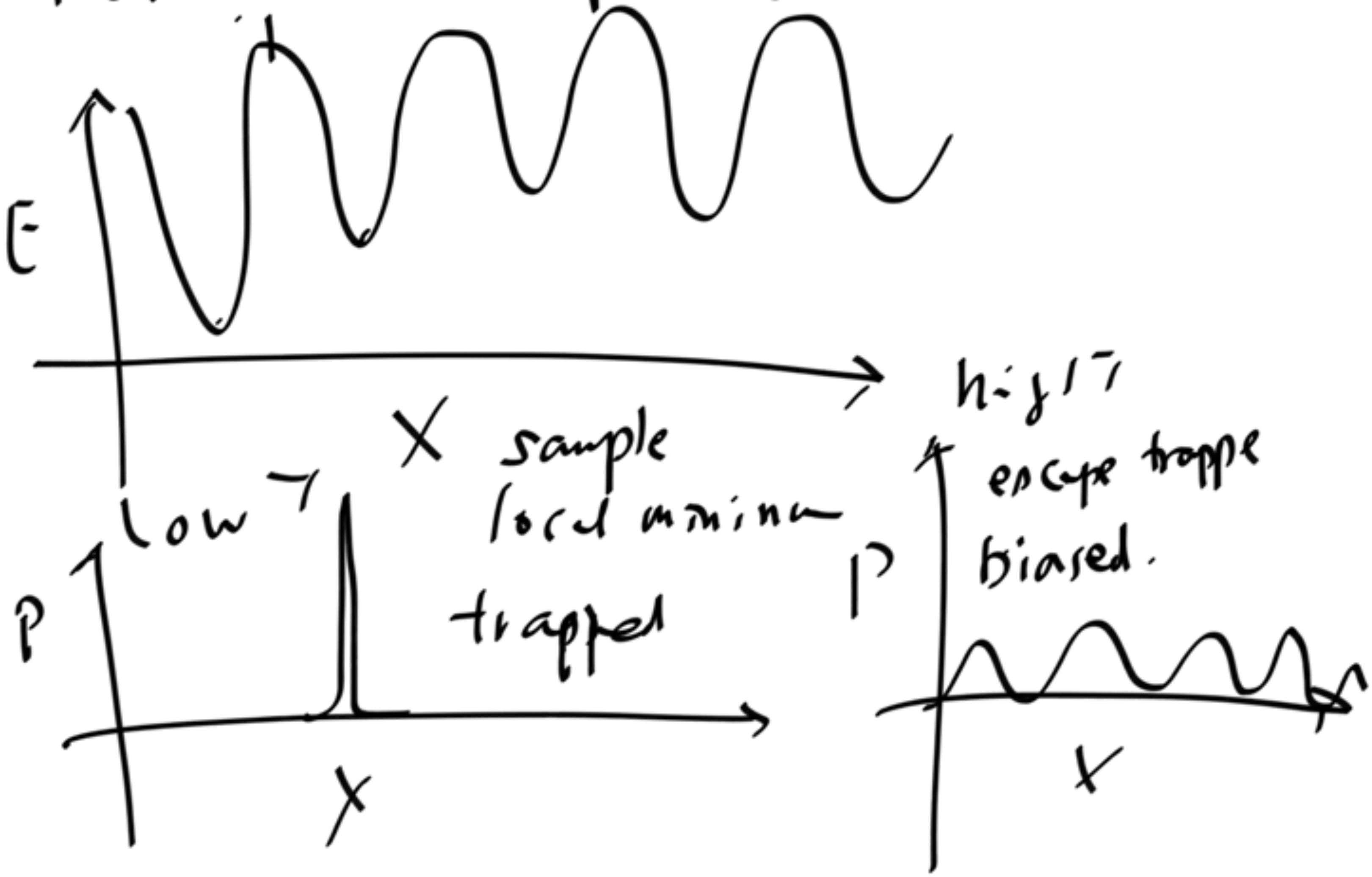
$$\mathrm{acc}(\vec{o} \to \vec{n}) = \min\left(1, \frac{W(\vec{n})}{W(\vec{o})}\right)$$

$$p(\vec{o}) \propto e^{-\beta U(\vec{o})} = e^{-\beta \sum_{i=1}^{\ell} u^{(i)}(o_j)}$$

$$p(\vec{n}) \propto e^{-\beta \sum_{i=1}^{\ell} u^{(i)}(n_j)}$$

$$p(\vec{o})\,\underline{\alpha(\vec{o}\to\vec{n})}\,acc(\vec{o}\to\vec{n})$$
$$= p(\vec{n})\,\alpha(\vec{n}\to\vec{o})\,acc(\vec{n}\to\vec{o})$$

Parallel tempering:



extended ensemble

$N\ \underline{\beta}\ V \qquad N\ V\ \beta_1$

$N\ V\ \beta_2$

$\vdots$

$N\ V\ \beta_n$

$$Q = \prod_{I=1}^{n} Q_I \ , \quad p(\vec{x}_1) = \frac{\frac{1}{h^{3N} N!} e^{-\beta U(\vec{x}_1)} \int d\vec{p}_1 e^{-\beta K(\vec{p}_1)}}{Q_I}$$

$$P(\vec{x}_1 | NV\beta_1, \vec{x}_2 | NV\beta_2, \dots)$$

$$= \prod_{I=1}^{n} \frac{1}{\underline{\underline{Q_I}}} \frac{1}{h^{3N} N!} e^{-\beta_I U(\vec{x}_I)} = \prod_{I=1}^{n} \frac{e^{-\beta_I U(\vec{x}_I)}}{Z_I}$$

$\frac{1}{h^{3N} N!} \times Z_I$

① for each ensemble, do MC
NVT at
$N\,V\,\beta_I$

② at regular interval, swap coordinate between ensemble i and j
with prob:

$$P(\vec{x}_1|\beta_1, \vec{x}_2|\beta_2, \ldots \vec{x}_i|\beta_i, \ldots, \vec{x}_j|\beta_j, \ldots) \, acc(\vec{o} \to \vec{n})$$

$$= P(\ldots\ldots\ldots \vec{x}_j|\beta_i, \ldots, \vec{x}_i|\beta_j, \ldots) \, acc(\vec{n} \to \vec{o})$$

$$\frac{acc(\vec{o} \to \vec{n})}{acc(\vec{n} \to \vec{o})} = e^{-(\beta_j - \beta_i)(U(\vec{x}_j) - U(\vec{x}_i))}$$

FE calculation:

$$\overset{NVT}{F} = -\frac{1}{\beta}\ln Q(N,V,T)$$

$$= -\frac{1}{\beta}\ln\frac{1}{\Lambda^{3N}N!}\int d\underline{\vec{q}}_N\, e^{-\beta U(\underline{\vec{q}}_N)}$$

$\because$ integral over conf space

$\therefore$ cannot be estimated accurately.

ΔF $\because$ F statefunction, depends only on current states, independent of how it is reached.