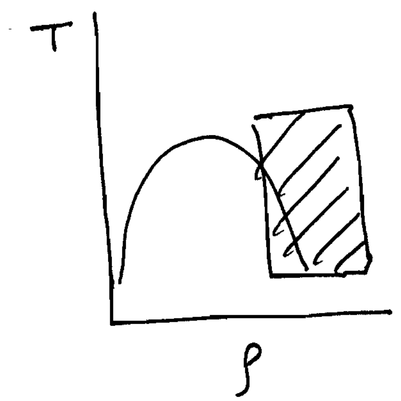
Flat Histogram Methods

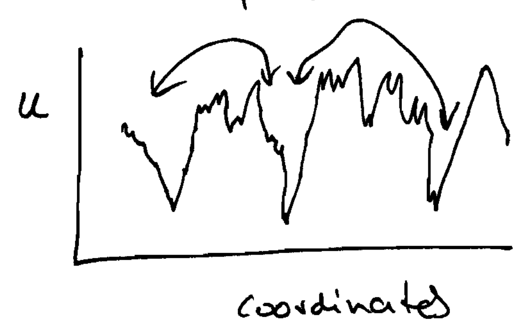
- Goal: obtain free energies to high accuracy
- Direct determination of thermodynamic potentials

$$S = k \ln \Omega$$

$$A = -kT \ln Q$$

- Broad Sampling of configurations





Canonical Simulations (NVT)

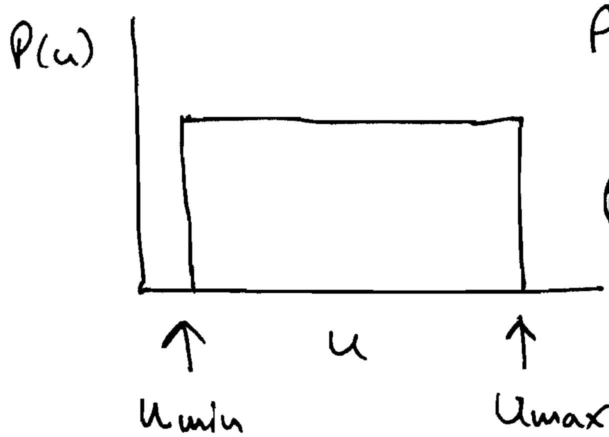
$$P(\vec{r}^N) \propto e^{-u/kT}$$

$$P(u) \propto \Omega(u) e^{-u/kT}$$

Flat Histograms

<u>no</u> temperature

Defined u_{min}, u_{max}



$$P(\vec{r}^N) \propto \frac{1}{\Omega(u)} = e^{-S(u)}$$

$$P(u) \propto \frac{\Omega(u)}{\Omega(u)} = \text{const.}$$

But... $\Omega(U)$ is unknown!

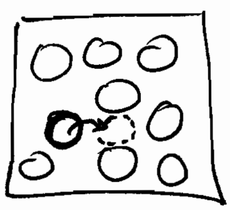
→ Accumulate probabilities of <u>visiting</u> microstates

[F. Wang - Landau DP, PRL <u>86</u>:2050 (2001)]

Also: Yan, Faller, de Pablo JCP <u>116</u>: 8745 (2002)
Shell, Debenedetti, A&P PRE <u>66</u>:056703 (2002)

Initialize: assume $S=0$ for all states

$g=1$ ("modification factor")



displacement move $\Delta\vec{r}$ uniform up to $|\Delta r_{max}|$

Acceptance criterion? [Detailed Balance]

$$P(old) \cdot \cancel{\alpha(old \to new)} \cdot Accept(old \to new) =$$
$$P(new)\, \cancel{\alpha(new \to old)} \cdot Accept(new \to old) \Rightarrow$$

$$\frac{Accept(old \to new)}{Accept(new \to old)} = \frac{P_{new}}{P_{old}} = \frac{1/\Omega(U_n)}{1/\Omega(U_o)} = \frac{\Omega(U_o)}{\Omega(U_n)}$$

Metropolis:

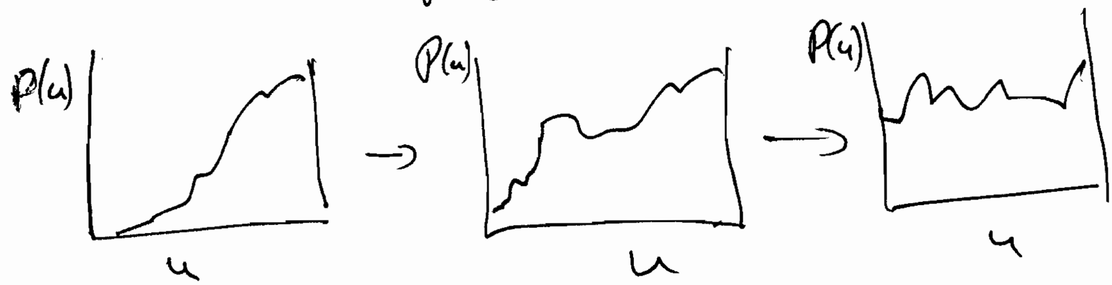
$$\boxed{Accept(old \to new) = \min\left\{1, \frac{\Omega(U_o)}{\Omega(U_n)}\right\}}$$

Since initially $S=0 \Rightarrow \Omega=1$ for all states, simulation will sample states of high U (high Ω) <u>more</u> than states of low U

keep track of (a) estimate of $\underline{\Omega}(u)$ by setting $\ln \underline{\Omega}(u_n) = \ln \underline{\Omega}(u_n) + g$ || Changing estimate of $\underline{\Omega}(u)$

(b) visited states $P(u)$ vs u

As sampling is increased:



If the $P(u)$ vs u histogram is "sufficiently flat" (e.g. $f = \dfrac{\text{max frequency}}{\text{min frequency}} < 2$) then

→ set $g \leftarrow g/2$

→ reset histogram $P(u)$

Repeat until g becomes smaller than a specified tolerance, g_{min} ($\simeq 10^{-3} - 10^{-5}$)

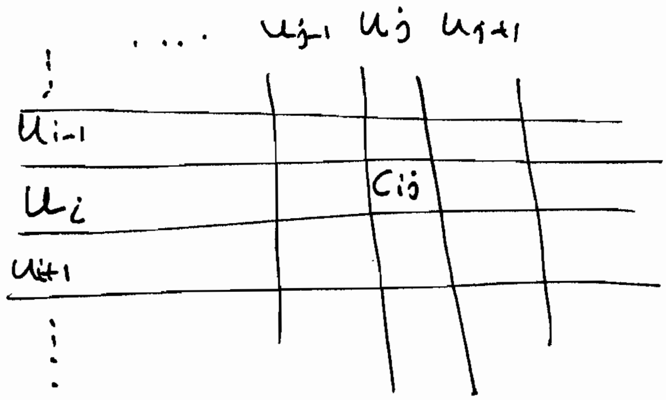
* Simulation does <u>not</u> satisfy detailed balance as $\underline{\Omega}(u)$ estimate is changing!
* Simple to implement
* Criterion for flatness of histograms affects quality of convergence
* States between U_{min} and U_{max} quickly sampled

<u>Disadvantage</u>: Limiting statistical quality, Inefficient use of simulation information

<u>Transition Matrix</u> J.S. Wang, R.H. Swendsen
J. Stat. Phys. <u>106</u>:245 (2001)

Probabilities of <u>proposed</u> moves between states:

$$\frac{P_{propose}(U_2 \to U_1)}{P_{propose}(U_1 \to U_2)} = \frac{\Omega(U_1)}{\Omega(U_2)}$$



C_{ij} : transition matrix

Accumulate during run:

For any proposed move $U_i \to U_j$

$$C(U_i, U_j) \leftarrow C(U_i, U_j) + 1$$

After many moves $\quad P_{propose}(U_i \to U_j) \simeq \dfrac{C(U_i, U_j)}{\sum_k C(U_i, U_k)}$

Estimate of $\Delta S = \dfrac{\Omega(U_2)}{\Omega(U_1)}$ from

$$P_{acc}(1 \to 2) = \exp(-\Delta S) = \frac{\Omega(U_1)}{\Omega(U_2)} = \frac{P_{propose}(2 \to 1)}{P_{propose}(1 \to 2)}$$

<u>Algorithm</u>: ① Initialize Transition matrix to zeros for all states

Algorithm (cont.) 2 Propose and accept/reject moves using the current value of

$$P_{acc} = \frac{P_{propose}(2 \to 1)}{P_{propose}(1 \to 2)}$$

3 Record proposed move in transition matrix

4 Stop when sufficient statistics have been gathered; generate $\Omega(u)$ from proposal probabilities

Discussion / Comparisons w/ W-L

* States are not uniformly sampled, can take time to visit less likely (low Ω) states
* Quality of results continues to improve

Combination: WL-TM: Shell et al., JCP 119:9406 (2003)

W-L propagation / quick sampling of states

TM estimation of $\Omega(u)$: more accurate, continuous improvement