

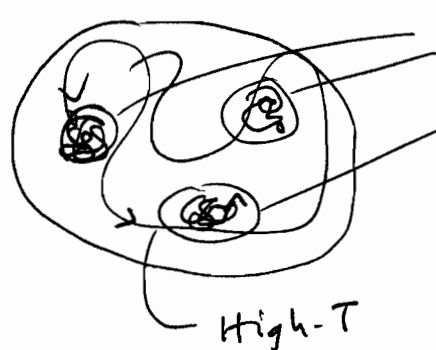
Parallel Tempering / Replica Exchange

References: §14.1 in f+S book

Earl+Deem, Phys.Chem.Chem.Phys. 7:3910 (2005).

Key concept: Simulate M replicas of a system, each at a different temperature.

→ High- T replicas allow for broad sampling of phase space; low- T ones allow for



low- T

detailed sampling of local (free) energy minima

→ Can be implemented on parallel clusters with little extra cost

Since replicas are not coupled,

$$Q = \prod_{i=1}^M \frac{1}{N_i^{3N} N!} \int d\vec{r}_i^N \exp[-\beta_i U(\vec{r}_i^N)]$$

Sampling within each replica done with NVT Monte Carlo (displacements, cluster moves) or MD at const. T (Nosé-Hoover, Andersen).

Periodically, swap configurations between nearby temperatures $T_{i,j}$ with probability

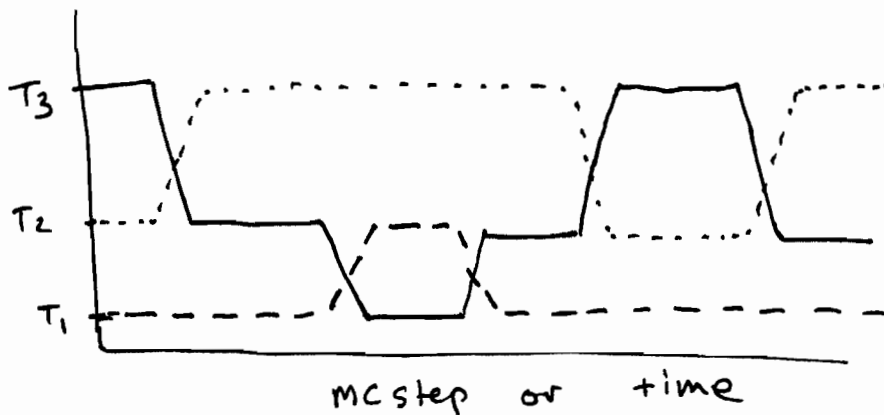
$$P_{acc} = \min \left\{ 1, \frac{\exp[-\beta_i U(\vec{r}_j^M) - \beta_j U(\vec{r}_i^M)]}{\exp[-\beta_i U(\vec{r}_i^M) - \beta_j U(\vec{r}_j^M)]} \right\} \Rightarrow$$

$$\Rightarrow P_{acc} = \min \left\{ 1, \exp \left[(-B_i + B_j) (U(\vec{r}_i^N) - U(\vec{r}_j^N)) \right] \right\}$$

(Note that i and j enter into this relationship in a symmetric way)

This acceptance criterion is written for MC, with only the configurational energy $U(\vec{r}^N)$ taken into account. For MD, as shown by Sugita + Okamoto, [Chem. Phys. Lett., 314:141 (1999)], the same criterion can be used, provided that the kinetic energies/velocities are rescaled to the new temperature:

$$v_i' = \sqrt{\frac{T_{new}}{T_{old}}} v_i \quad \text{for any replica being exchanged}$$



How do we select the temperature interval + spacing?

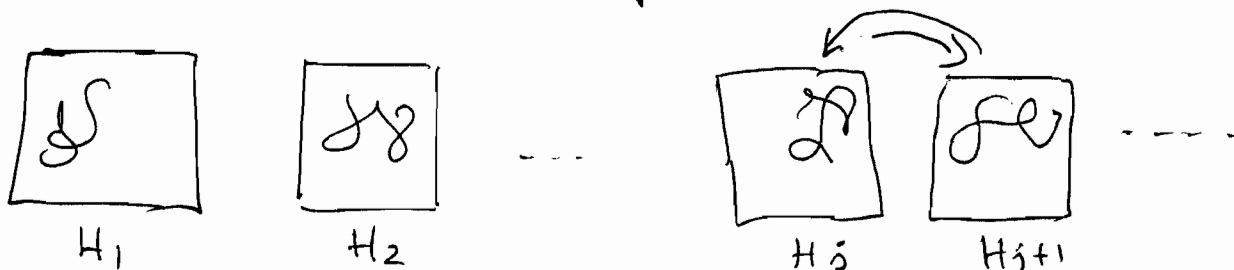
→ T_{min} , T_{max} based on range of interest; T_{max} should be sufficiently high to sample broad region of configuration space

→ Geometric spacing: $\frac{T_{i+1}}{T_i} = \text{const.}$

→ adjust # of intervals to give 20-25% acceptance of swaps

Other options :

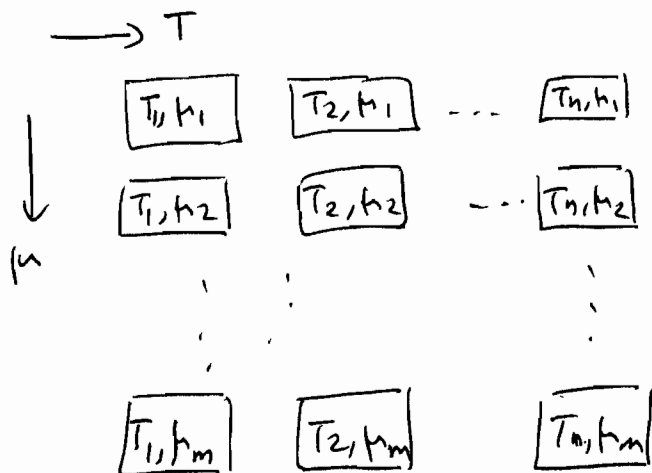
- * Scaling Hamiltonians
- * multidimensional - e.g. (h, T) replicas



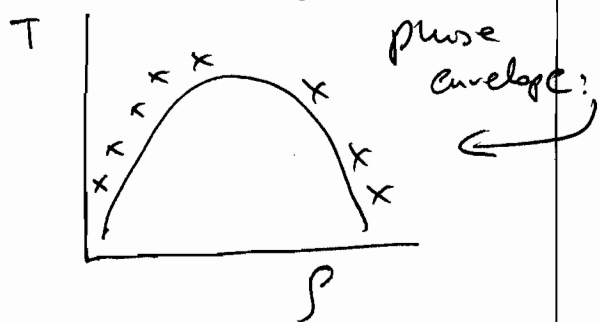
$H_1, H_2 \dots H_j \dots$: different Hamiltonians (e.g. strength of hydrophobic or electrostatic interactions)

$$P_{acc} = \min \left\{ 1, \exp \left[-\beta \left([H_i(\vec{r}_i^N) + H_j(\vec{r}_i^N)] - [H_i(\vec{r}_i^N) + H_j(\vec{r}_j^N)] \right) \right] \right\}$$

Faller, Yan + de Pablo JCP 118:5419 (2002)



GCMC at multiple states, usually around



Configuration $m @ T_i, h_i$
 $n @ T_j, h_j$ } swap attempt

$$P_{acc} = \min \left\{ 1, \exp \left[-(\beta_i - \beta_j)(E_n - E_m) + (\beta_i h_i - \beta_j h_j)(N_n - N_m) \right] \right\}$$

The main difficulty in swapping is the degree of overlap of the relevant configurations.

Degree of overlap can be increased by using an "umbrella potential" to broaden range of sampled states ("multicanonical" simulations)

$$P(\vec{r}^N) = (\text{const}) \cdot e^{-\beta U(\vec{r}^N)} \cdot w(\vec{r}^N)$$

↑

umbrella sampling potential

Torrie + Valleau, J. Comput. Phys. 113: 6042 (2000).

$$\left[\text{If } w(\vec{r}^N) = \exp[-u + TS] \text{ umbrella sampling} \right]$$

$w(\vec{r}^N)$ can be obtained from short preliminary simulations