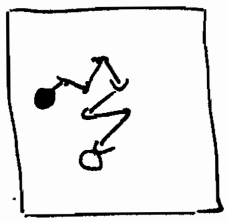
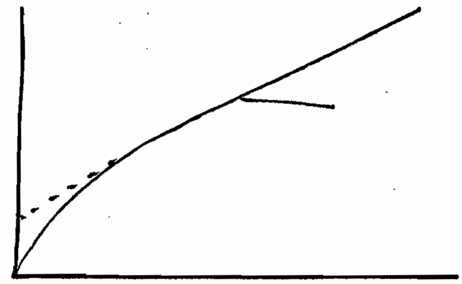
Connection between MC steps and dynamics





How do we translate from # of MC steps to "real" time? Do we assume that each MC step corresponds to a certain sized amount of time τ?

States: m (old)
n (new)

$\rho(m,t)$: probability of system being in state m at time t

$$\frac{d\rho(m,t)}{dt} \simeq -\sum_n \frac{\Gamma(m\to n)}{\tau}\rho(m,t) + \sum_n \frac{\Gamma(n\to m)}{\tau}\rho(n,t)$$

We know that $$\rho(m,\infty) = \frac{\exp(-\beta E_m)}{\sum_n \exp(-\beta E_n)}$$

As we have discussed earlier, there are several different choices for the transition probabilities that satisfy detailed balance at equilibrium:

$$\frac{d\rho(m,\infty)}{dt} = 0 \Rightarrow \sum_m \Gamma(m\to n)\rho(m,\infty) = \sum_m \Gamma(n\to m)\rho(n,\infty)$$

Different choices will result in different dynamics (effective diffusion coefficients, temperature dependence)

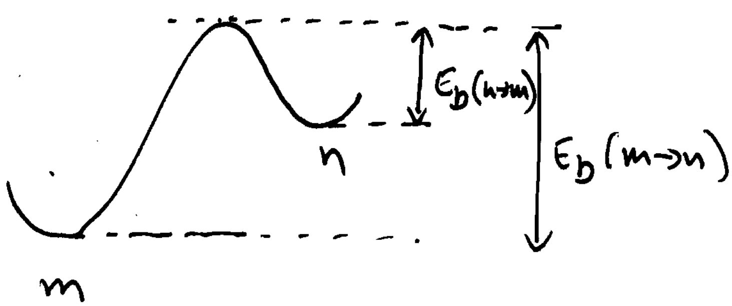
1) Metropolis Dynamics

$$\Pi_{Met}(m \to n) = \exp(-\Delta E/kT) \qquad \Delta E > \phi$$
$$= 1 \qquad \Delta E \leq \phi$$

2) Kawasaki Dynamics (Kawasaki, 1966)

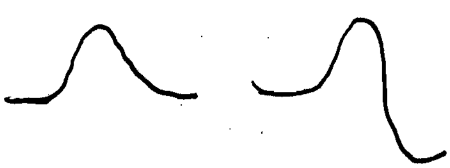
$$\Pi_{Kaw}(m \to n) = \frac{\exp(-\Delta E/2kT)}{\exp(-\Delta E/2kT) + \exp(\Delta E/2kT)} = \frac{\exp(-\frac{\Delta E}{kT})}{1 + \exp(-\frac{\Delta E}{kT})}$$

3) "Thermally excited" dynamics (Kang + Weinberg, 1989)



$$\Pi_{T.E.D.}(m \to n) = $$
$$= \exp\left(-\frac{E_b(m\to n)}{kT}\right)$$

If the activation energy barrier between any two states is the same, irrespective of their energy difference, then thermally excited dynamics reduce to Metropolis dynamics, except for a trivial factor of $\exp\left(-\frac{\delta E}{kT}\right)$ — assuming no reverse crossings!



If the possibility of reverse barrier crossings is included, which is more realistic, with other assumptions being the same, we recover Kawasaki dynamics.

How do we select time step τ?

Typical dynamical processes occuring through distinct "jumps" cannot be easily described by an MC process in which a step is equivalent to a fixed amount of time:

characteristic time for jump $\tau_j = \frac{1}{r}$

rate, events /s

If a Monte Carlo step covers time τ_{mc},

if $\tau_{mc} \ll \tau_j$ → prob. of acceptance is too low, slow evolution

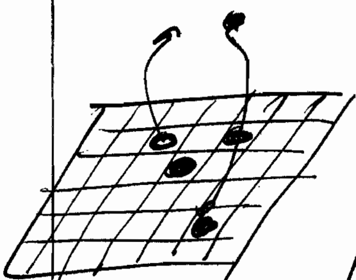
$\tau_{mc} \gtrsim \tau_j$ → more than one events can occur during time τ_{mc}

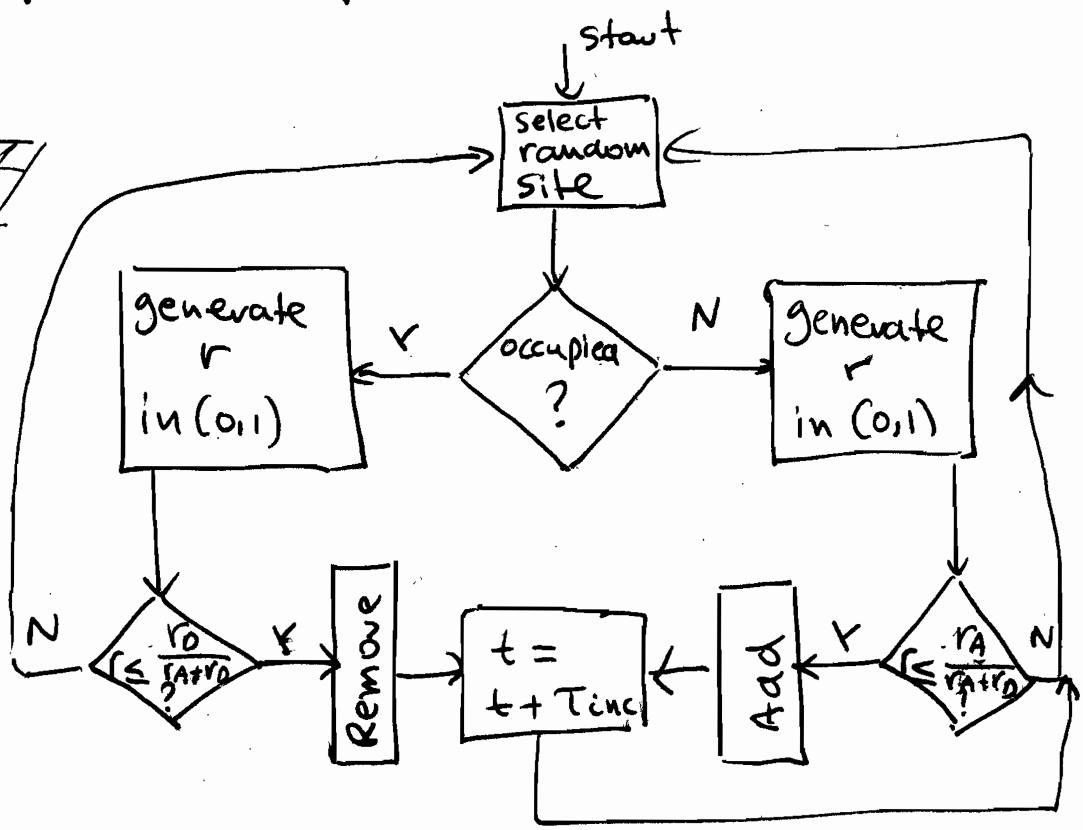
Solution: (Fichthorn + Weinberg, 1991) → construct Poisson Process

Example: Adsorption–desorption equilibrium

$$\frac{d\theta}{dt} = \underbrace{r_A(1-\theta)}_{\text{adsorption}} - \underbrace{r_D\theta}_{\text{desorption}} \quad \text{(Langmuir isotherm)}$$

adsorption desorption rates





τ_{incr}, the time increment for trial i is selected from an exponential distribution with rate

$$\underbrace{r_i}_{\text{rate @}i} = \underbrace{N}_{\#\text{ of total sites}} \cdot \left[(1-\theta_i) r_A + \theta_i r_D \right]$$

$$\tau_i = -\frac{1}{r_i} \ln(\xi) \qquad \xi: \text{ random number between } 0 \text{ and } 1$$