Transition Path Sampling

based on notes from CHEM295, 23 April 2009, taught by Phill Geissler

First, we consider the probability distribution for a (discretized) trajectory $x(\tau) = \{x_0, x_{\Delta t}, \ldots, x_{\tau-\Delta t}, x_\tau\}$:

$$P[x(\tau)] = \rho(x_0) \prod_{i=0}^{(\tau-\Delta t)/\Delta t} \pi(x_{i\Delta t} \to x_{(i+1)\Delta t}) \qquad (i)$$

where $\rho(x_0)$ is the probability (at equilibrium) of having the initial condition x_0 and $\pi(x_{t_1} \to x_{t_2})$ is the probability (for a given dynamics) that a system in state x_{t_1} at time t_1 will be in state x_{t_2} at time $t_2 > t_1$.

In order to focus on reactive trajectories, we multiply ~~by~~ the characteristic functions, requiring that the system be in state A at time 0 and state B at time τ:

$$P_{rxn}[x(\tau)] \propto P[x(\tau)]\, h_A(x_0)\, h_B(x_\tau) \qquad (ii)$$

Now we would like to do Monte Carlo by importance sampling in the subset of reactive trajectories. We start by developing a technique that will satisfy detailed balance:

Detailed Balance:

We start with the Metropolis acceptance criterion (which will always satisfy detailed balance):

$$acc(o \to n) = \min\left(1, \frac{P(n)}{P(o)} \frac{\alpha(n \to o)}{\alpha(o \to n)}\right) \qquad (iii)$$

where $P(i)$ is the probability of being in (micro)state i, and $\alpha(i \to j)$ is the probability of generating (micro)state j given that we begin in (micro)state i. Plugging in the reactive trajectory probability from (ii) and the definition in (i), we obtain

$$acc(o \to n) = \min\left(1, \frac{\rho(x_0^n)}{\rho(x_0^o)} \frac{\prod_{i=0}^{(\tau-\Delta t)/\Delta t} \pi(x_{i\Delta t}^n \to x_{(i+1)\Delta t}^n)}{\prod_{i=0}^{(\tau-\Delta t)/\Delta t} \pi(x_{i\Delta t}^o \to x_{(i+1)\Delta t}^o)} \frac{h_A(x_0^n)\, h_B(x_\tau^n)}{1} \frac{\alpha(n \to o)}{\alpha(o \to n)}\right) \qquad (iv)$$

where we assume that the old trajectory is reactive; i.e. $h_A(x_0^o)\, h_B(x_\tau^o) = 1$.

This still leaves us needing the generation probability, $\alpha(o \to n)$, which will depend on the algorithm.

The Shooting Algorithm:

The basic idea of the shooting algorithm is to pick a time on the existing trajectory and to make a small perturbation to the velocity at that time, from which a new (perturbed) trajectory is generated. The probability of generating a given new trajectory is therefore:

$$\alpha(o \to n) = (\text{probability of choosing time } t)(\text{prob. of } \Delta v)(\text{prob of fwd traj})(\text{prob of backward traj})$$
$$= P(t)P(\Delta v) \prod_{i=0}^{(\tau-t-1)/\Delta t} \pi(x^n_{t+i\Delta t} \to x^n_{t+(i+1)\Delta t}) \prod_{i=0}^{(t-1)/\Delta t} \bar{\pi}(x^n_{t-i\Delta t} \to x^n_{t-(i+1)\Delta t}) \qquad (v)$$

where $\bar{\pi}(x_{t_1} \to x_{t_2})$ works like $\pi(x_{t_1} \to x_{t_2})$, but for cases where $t_2 < t_1$.

Now we make assumptions about the chosen dynamics. If the dynamics satisfy the principle of microscopic reversibility, then we have

$$\frac{\bar{\pi}(x \to x')}{\pi(x' \to x)} = \frac{\rho(x')}{\rho(x)} \quad \Rightarrow \quad \bar{\pi}(x \to x') = \pi(x' \to x)\,\frac{\rho(x')}{\rho(x)}$$

Now we can describe the backward dynamics in terms of the forward dynamics, making eqn (v) into:

$$\alpha(o \to n) = P(t)P(\Delta v) \prod_{i=0}^{(\tau-t-1)/\Delta t} \pi(x^n_{t+i\Delta t} \to x^n_{t+(i+1)\Delta t}) \prod_{i=0}^{(t-1)/\Delta t} \pi(x^n_{i\Delta t} \to x^n_{(i+1)\Delta t})\,\frac{\rho(x^n_{i\Delta t})}{\rho(x^n_{(i+1)\Delta t})}$$
$$= P(t)P(\Delta v) \prod_{i=1}^{(\tau-t-1)/\Delta t} \pi(x^n_{t+i\Delta t} \to x^n_{t+(i+1)\Delta t}) \prod_{i=0}^{(t-1)/\Delta t} \pi(x^n_{i\Delta t} \to x^n_{(i+1)\Delta t}) \quad \frac{\rho(x^n_0)}{\rho(x^n_t)}$$
$$= P(t)P(\Delta v)\,\frac{\rho(x^n_0)}{\rho(x^n_t)} \prod_{i=0}^{(\tau-1)/\Delta t} \pi(x^n_{i\Delta t} \to x^n_{(i+1)\Delta t}) \qquad (vi)$$

Assuming symmetric selections of $P(t)$ and $P(\Delta v)$, this gives us an acceptance rule

$$acc(o \to n) = \min\left(1,\ \frac{\rho(x^n_0)}{\rho(x^o_0)} \cdot \frac{\prod_{i=0}^{t-1} \pi(x^n_{i\Delta t} \to x^n_{(i+1)\Delta t})}{\prod_{i=0}^{t-1} \pi(x^o_{i\Delta t} \to x^o_{(i+1)\Delta t})} \cdot h_A(x^n_0)h_B(x^n_\tau) \cdot \frac{P(t)P(\Delta v)}{P(t)P(\Delta v)} \cdot \frac{\rho(x^o_0)}{\rho(x^o_t)} \cdot \frac{\rho(x^n_t)}{\rho(x^n_0)} \cdot \frac{\prod_{i=0}^{(\tau-1)/\Delta t} \pi(x^o_{i\Delta t} \to x^o_{(i+1)\Delta t})}{\prod_{i=0}^{(\tau-1)/\Delta t} \pi(x^n_{i\Delta t} \to x^n_{(i+1)\Delta t})}\right)$$
$$= \min\left(1,\ h_A(x^n_0)h_B(x^n_\tau)\,\frac{\rho(x^n_t)}{\rho(x^o_t)}\right)$$

If we can further assume that $\rho(x^n_t) = \rho(x^o_t)$ (as it will if Δv conserves kinetic energy and if the dynamics are Newtonian), then we obtain the simple result:

$$acc(o \to n) = h_A(x^n_0)\,h_B(x^n_\tau).$$