Canonical Sampling

So far, we have seen that if we integrate Newton/Hamilton's Equations of Motion, then we conserve total energy

$$\mathcal{H} = K.E. + P.E$$

This means we sample the canonical ensemble, where all states are equally likely

$$\Omega \propto \int d\vec{p} \int d\vec{q}\, \delta(\mathcal{H}(\vec{p},\vec{q}) - E)$$

But we also know that we are much more interested in (N,V,T), (or (N,P,T))

How can we do this in Simulation?

One way was MC, where we saw how we can use Metropolis rule to satisfy $P(\underline{X}) \propto e^{-\beta \mathcal{H}(\underline{x})}$

Advantages & disadvantages of MC vs MD, but there are good reasons to like MD

Note:
discussed hybrid MC here

So how can we do this? Many solutions...
Some preserve $P(\underline{X} = (p,q)) \propto e^{-\beta \mathcal{H}(p,q)}$
and some only preserve $P(\vec{q}) \propto e^{-\beta U(\vec{q})}$
(which is often what we care about)

Simple approaches - don't necessarily perfectly give canonical sampling

1) T rescaling $\langle \frac{1}{2} m v^2 \rangle = \frac{3}{2} k_B T$

$$\frac{\frac{1}{2} m v_{ideal}^2}{\frac{1}{2} m v_{current}^2} = \frac{T}{T_{current}}$$

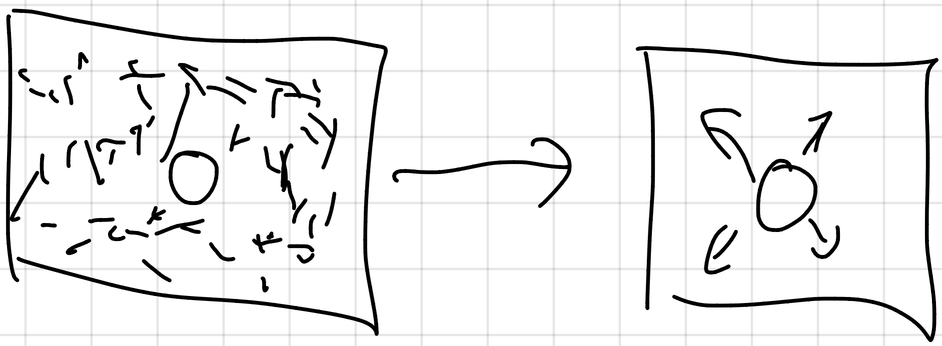
so $v_{ideal} = \sqrt{T / T_{current}}\, v_{current}$

2) Better, sample v's from maxwell Boltzmann dist
(random velocities though means lose inertia)
$\Rightarrow$ canonical momentum dist

3) Reset a subset with frequency ν
so if random $< \nu \Delta t$, resample
(Andersen)

Better solutions can be proved to give canonical sampling

Solution! Langevin Dynamics Inspired by Brownian motion ~



Effectively looks like random forces from surroundings and drag of going through medium

$$\Rightarrow \quad F_i(x) = -\nabla U(x) - \gamma v(t) + F_i^{random}(x,t)$$

$$\text{or} \quad m\dot{v} = -\nabla U(x) - \gamma v(t) + F_i^{random}(x,t)$$

$$\Rightarrow \quad \frac{dv}{dt} = -\frac{1}{m}\nabla U(x) - \gamma/m \, v(t) + \frac{1}{m}F_i^{random}(x,t)$$

Want: random force adds energy and drag removes energy such that $P(x)$ sampled @ right temp if random, shouldn't depend on position or on time → way this is written is [white noise]

$$\langle F(t) \rangle = 0$$

$$\langle F(t) F(t') \rangle = 2\gamma k_B T \ \delta(t-t')$$

(variance)

In practice

$$dq/dt = v dt$$

$$F = -\nabla U(x) - \gamma m v(t) + \sqrt{2\gamma k_B T m}\, R(t)$$

Where $R(t)$ is a random number from $\sim \mathcal{N}(0,1)$

and use this in Verlet equations

Leimkuhler & Mathews [~2013]

showed

$$\underbrace{\begin{bmatrix} dq \\ dp \end{bmatrix} = \begin{bmatrix} p/m \\ 0 \end{bmatrix} dt}_{A} + \underbrace{\begin{bmatrix} 0 \\ -\nabla U(q) \end{bmatrix} dt}_{B} + \underbrace{\begin{bmatrix} 0 \\ -\gamma p\, dt + \sqrt{2\gamma k_B T m}\, dW \end{bmatrix}}_{O}$$

That doing $[BAOA]^n$ or BAOAB method is most robust method for sampling accurately

can use very low γ and still get good sampling, least wasted time

Another important limit is "Brownian Dynamics", aka "overdamped Langevin dynamics", no inertia $\gamma \to \infty$. w/ no random force for a min

$\Rightarrow$ $m\frac{dv}{dt} \approx \gamma v$, $v(t) = v(0)e^{-\gamma/m\, t}$ $\to$ stops by fluid immediately

In this limit $p \approx 0$ and hence $dp/dt \approx 0$

then $0 = -\nabla U dt - \gamma M \underline{v\, dt} + \sqrt{2\gamma k_B T m}\, R(t)$

and $dq = v\,dt$

so $dq = -\frac{\nabla U}{\gamma M} dt + \sqrt{\frac{2k_BT}{\gamma M}}\, R(t)$ [Really easy to simulate]

Idea 2 Microcanonical Sampling but add extra fake position & momentum.

(Done in a special way to make other states sampled correctly)

Idea by Nosé (1983, 84), checks whether KE too high or low & rescales continuously

$$[\mathcal{E}] = [p_s]^2/[Q]$$
$$[p_s] = [\partial\mathcal{L}/\partial\dot{s}] = [\mathcal{E}]$$

thigh mass = strong control

$$\mathcal{H}_N = \sum_{i=1}^{N} \frac{p_i'^2}{2m_i \underbrace{s^2}_{\text{rescale}}} + U(\vec{q}) + \overbrace{\frac{p_s^2}{2Q} + \underbrace{g k_B T \ln s}_{\text{potential in } s}}^{\text{extra}}$$

Q determines timescale over which rescaling happens on avg, and has units $[\mathcal{E}][t]^2$

$2dN+2$ dimensions (s has to be positive)

g will ensure canonical sampling

$$\Omega = \int dq^{dN} \int dp'^{dN} \int ds \int dp_s \, \delta(\mathcal{H}(\vec{p}', \vec{q}, s, p_s) - \mathcal{E})$$

define $p_i = p_i'/s$

$$= \int dq^{dN} \int dp^{dN} \int ds \int dp_s \, s^{dN} \delta(\mathcal{H}_{phys}(p,q) + p_s^2/2Q + g k_B T \ln s - \mathcal{E})$$

$$\mathcal{H}_{phys}(\vec{p}, \vec{q}) = \sum_{i=1}^{N} p_i^2/2m + U(\vec{q})$$

$$f(s) \equiv \mathcal{H} + p_s^2/2Q + g k_B T \ln s - \mathcal{E}$$

$$f(s_0) = 0 \Rightarrow g k_B T \ln s_0 = \mathcal{E} - \mathcal{H} + p_s^2/2Q \Rightarrow s_0 = e^{\frac{-1}{g k_B T}(\mathcal{H} + p_s^2/2Q - \mathcal{E})}$$

$$\delta(f(s)) = \delta(s - s_0) / |f'(s_0)| \quad \text{if } f(s_0) = 0 \text{ is only zero of } f$$

$$df/ds\Big|_{s_0} = \frac{g k_B T}{s_0} = g k_B T \, e^{+\frac{1}{g k_B T}(\mathcal{H} + p_s^2/2Q - \mathcal{E})}$$

$$\Rightarrow \Omega = \int dp'^{dN} \int dq^{dN} \int ds \int dp_s \; \underbrace{s^{dN} \delta(s-s_0)}_{s_0^{dN}} \cdot \frac{1}{g k_B T} e^{[\mathcal{E} - \mathcal{H} - p_s^2/2Q]/g k_B T}$$

$$= \int dp^{dN} \int dq^{dN} \int dp_s \frac{1}{g k_B T} e^{(dN+1)/g k_B T \, [\mathcal{E} - \mathcal{H} - p_s^2/2Q]}$$

$$g = dN+1$$

$$= \int dp^{dN} \int dq^{dN} \int dp_s \cdot \underbrace{\frac{1}{(dN+1) k_B T}}_{\text{const}} e^{\beta \mathcal{E}} e^{-\beta \mathcal{H}} \underbrace{e^{-\beta p_s^2/2Q}}_{\int = \sqrt{2\pi Q/\beta}}$$

$$= \frac{e^{\beta \mathcal{E}} \sqrt{2\pi k_B T Q}}{(dN+1) k_B T} \int dp^{dN} \int dq^{dN} e^{-\beta \mathcal{H}(\vec{p}, \vec{q})}$$

$$\propto Q(N, V, T)$$

So what are the dynamics that do this sampling

$$\frac{dq_i}{dt} = \frac{\partial \mathcal{H}_N}{\partial p_i'} = \frac{p_i'}{m_i s^2} \qquad \frac{dp_i'}{dt} = -\frac{\partial \mathcal{H}_N}{\partial q_i} = F_i$$

$$\frac{ds}{dt} = \frac{\partial \mathcal{H}}{\partial p_s} = p_s/Q \qquad \frac{dp_s}{dt} = -\frac{\partial \mathcal{H}}{\partial s} = \sum_{i=1}^{N} \frac{p_i'^2}{m s^3} - \frac{g k_B T}{s}$$

$$= \frac{1}{s}\left[\underbrace{\sum_{i=1}^{N} p_i'^2/m s^2 - g k_B T}\right]$$

p_s changed based on if 2x fake KE is

bigger or smaller than $(2dN+1)k_BT$

replace $p_i = p_i'/s$, $\bar{p}_s = p^s/s$ & $d\bar{t} = dt/s$

$\partial q/d\bar{t} = p_i/m_i$ $\quad$ $dp/d\bar{t} = F - s\bar{p}_s/Q\, \bar{p}_i$

$ds/d\bar{t} = s^2\, \bar{p}_s/Q$ $\quad$ $d\bar{p}_s/d\bar{t} = 1/g\left[\sum p^2/2m - gkT\right] - sp_s^2/Q$

(Time scaled, "non canonical transformation")

Nosé - Hoover, Start w/ Nosé &

$p_i = p_i'/s$ $\quad$ $d\bar{t} = dt/s$ $\quad$ $\frac{1}{s}\, ds/dt' = d\eta/dt'$ $\quad$ $p_s = p_\eta$

& $g = dN$

$\frac{dq_i}{dt} = p_i/m_i$ $\quad$ $\frac{dq_i}{dt} = F_i - p_\eta/Q\, p_i$

$d\eta/dt = p_\eta/Q$ $\quad$ $dp_\eta/dt = \sum_{i=1}^{N} p_i^2/m_i - dNk_BT$

(η from Martyna, 1992)

* Non-Ergodic for simple harmonic oscillator