# Constant temperature Simulation

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 $P(\bar{X}) \propto e^{-\beta \mathcal{H}(\bar{x})}$

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

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

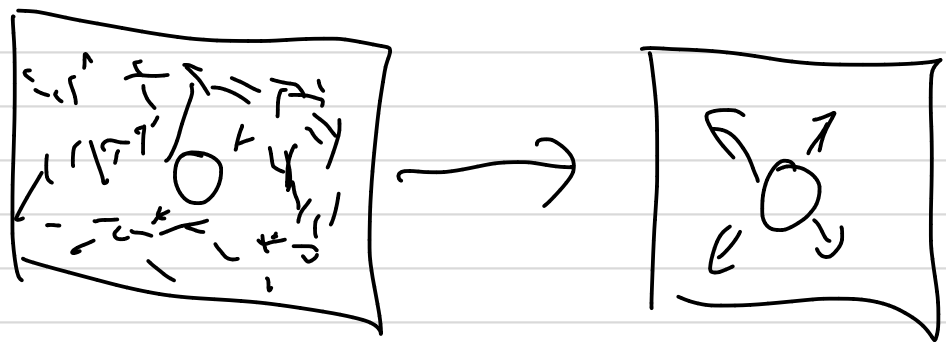
3) Reset a subset with frequency $\nu$

so if random $< \nu \Delta t$, resample

(Anderson)

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

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

(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

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

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

can use very low $\gamma$ 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

$\Rightarrow m\frac{dv}{dt} \approx \gamma v$ , $v(t) = v(0)e^{-\gamma/m\, t}$ → 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

High mass = strong control

$[\varepsilon] = [p_s]^2/[\varepsilon Q]$

$[p_s] = [\frac{\partial \mathcal{H}}{\partial \dot{s}}] = [\varepsilon]$

extra

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

rescale

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

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

g will ensure canonical sampling

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

define $p_i = p_i'/s$

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

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

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

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

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

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

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

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

$g \equiv 2d+1$

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

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

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

So what are the dynamics that do this sampling

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

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

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

$p_s$ changed based on if 2x fake KE is

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

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

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

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

(Time scaled, "non canonical transformation")

---

Nosé - Hoover, Start w/ Nosé &

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

& $g = dN$

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

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

($\eta$ from Martyna, 1992)

★ Non-Ergodic for simple harmonic oscillator