**Canonical Sampling**

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

\[ H = kE + pE \]

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

But we also know that we are much more interested in \((N,U,T)\) 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

\[ P(X) \propto e^{-\beta H(X)} \]

Advantages & disadvantages of MC vs MD, but there are good reasons to (like MD)
Note: discussed hybrid me here

So how can we do this? Many solutions...

Some preserve $P(\mathbf{X} = (p, q)) \propto e^{-\beta H(p, q)}$

and some only preserve $P(\mathbf{q}) \propto e^{-\beta U(q)}$

(which is often what we are after)

Simple approaches - don't necessarily perfectly
give canonical sampling

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

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

so $v_{\text{ideal}} = \sqrt{\frac{T}{T_{\text{current}}}} v_{\text{current}}$

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 $U$

so if random $< U A t$, 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:

\[ F_i(x) = -\nabla U(x) - \sigma v(t) + F_{i,\text{random}}(x,t) \]

Corresponding:

\[ m \frac{dv}{dt} = -\nabla U(x) - \sigma/m v(t) + \frac{1}{m} F_{i,\text{random}}(x,t) \]

Want: random force adds energy and drag removes energy such that \( P(x) \) sampled at right temp.
If random, shouldn't depend on position or on time \( \rightarrow \) in this as written is \( \text{[white noise]} \)

\[
\langle F(t) \rangle = 0 \\
\langle F(t)F(t') \rangle = 2\sigma k_b T \delta(t-t')
\]

(Variance)

In practice
\[
dp/dt = vdt
\]

\[
F = -\nabla U(x) - mV(t) + \sqrt{2\sigma k_b T m} R(t)
\]

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

and use this in Verlet equations

Leimkuhler & Matthews \[\sim 2013\]

Showed
\[
\begin{bmatrix}
\frac{dp}{dt} \\
\frac{dx}{dt}
\end{bmatrix} =
\begin{bmatrix}
p/m \\
0
\end{bmatrix} dt + 
\begin{bmatrix}
0 \\
-\nabla U(x)
\end{bmatrix} dt + 
\begin{bmatrix}
0 \\
\sqrt{T/m k_b T} R(t)
\end{bmatrix}
\]

That doing \([BAOA]^{n}\) or \(BAOAB\) method is

most robust method for sampling accurately

can use very low \( \sigma \) 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 \( \sim \) min.

\[ m \frac{dy}{dt} \sim -6v, \quad v(t) = v(0) e^{-\gamma mt} \rightarrow \text{stop by fluid immediately} \]

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

then \[ \dot{q} = -\nabla U \dot{q} - 6 M v dt + \sqrt{2k_b T m \rho} \dot{q} \]

and \[ dq = v dt \]

so \[ dq = -\frac{\nabla U}{\rho} dt + \sqrt{\frac{2k_b T \rho}{\rho}} \dot{q} \rightarrow \text{[Really easy to simulate]} \]

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Idea 2: Microcanonical sampling but add extra, fake position & momentum.

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

Idea by Nose (1983, 84), checks whether KE too high or too low & rescales continuously
\[ H_N = \sum_{i=1}^{N} \left( \frac{p_i^2}{2m} + U(q_i) \right) + \frac{P_s^2}{2Q} + g k_B T \ln s \]

A determines timescale over which rescaling happens. \( H_N \) is in units \([E][+g^2\mu]\). 

**g** will ensure canonical sampling.

\[ R = \int d\theta d\phi \left[ \int d^3p d^3q \right] S(H(p, q) - \mathcal{E}) \]

Define \( \rho_i = \frac{\rho_i}{s} \)

\[ = \int d\theta d\phi \left[ \int d^3p d^3q \right] S\left( \frac{H(p, q)}{p_i} \mathcal{E} + \frac{p_i^2}{2m} + g k_B T \ln s - \mathcal{E} \right) \]

\[ H_{\text{phys}} \left( \frac{\rho}{q}, \mathcal{E} \right) = \sum_{i=1}^{N} \frac{p_i^2}{2m} + U(q_i) \]

\[ f(s) \equiv H + \frac{P_s^2}{2Q} + g k_B T \ln s - \mathcal{E} \]

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

\[ S(f(s)) = \frac{s(s-s_0)}{f'(s_0)} \left| f'(s_0) \right| \text{ if } f(s_0) = 0 \text{ is only zero of } f \]

\[ \frac{df}{ds} \bigg|_{s_0} = g k_B T \frac{1}{s_0} = g k_B T e^{-\frac{1}{g k_B T}(H + \frac{P_s^2}{2Q} - \mathcal{E})} \]
\[ S_{\mathcal{L}} = \int dp_{1} dp_{2} dp_{3} \cdot \frac{1}{g_{k_{B}T}} e^{-\frac{E(s-s_{0})}{g_{k_{B}T}}} \]

\[ = \int dp_{1} dp_{2} dp_{3} \cdot \frac{1}{g_{k_{B}T}} e^{-\frac{c_{N+1} E(s-s_{0})}{g_{k_{B}T}}} \]

\[ g = dN + 1 \]

\[ = \int dp_{1} dp_{2} dp_{3} \cdot \frac{1}{g_{k_{B}T}} e^{-\frac{c_{N+1} E(s-s_{0})}{g_{k_{B}T}}} \]

\[ = e^{\frac{c_{N+1} E(s-s_{0})}{g_{k_{B}T}}} \int dp_{1} dp_{2} dp_{3} e^{-\frac{c_{N+1} E(s-s_{0})}{g_{k_{B}T}}} \]

\[ \approx \mathcal{Q}(N, N, T) \]

So what are the dynamics that do this sampling:

\[ \frac{d\hat{q}_{i}}{dt} = \frac{\partial H}{\partial \hat{p}_{i}} = \frac{P_{i}}{m} \text{ s}^{-2} \]

\[ \frac{d\hat{p}_{i}}{dt} = -\frac{\partial H}{\partial \hat{q}_{i}} = F_{i} \]

\[ \frac{dS}{dt} = \frac{\partial S}{\partial \hat{p}_{s}} = \frac{P_{s}}{g_{k_{B}}} \]

\[ \frac{d\hat{p}_{s}}{dt} = -\frac{\partial S}{\partial \hat{q}_{s}} = \frac{N}{g_{k_{B}}} \frac{\hat{p}_{s}^{2}}{m_{s}^{2}} - \frac{g_{k_{B}}}{2} \]

\[ = \frac{1}{2} \left[ \frac{\sum_{i=1}^{N} \frac{\hat{p}_{i}^{2}}{m_{i}^{2}}}{g_{k_{B}}} \right] - \frac{g_{k_{B}}}{2} \hat{q}_{s} \]

Ps changed based on if 2x fake KE is
bigger or smaller than \((2dN + 1)k_B T\)

Replace \( p_i = p_i'/s \), \( s = p_i''/s \) & \( dT = dT'/s \)

\[
\frac{d\dot{p}_i}{dT} = \frac{p_i'}{m_i} \quad \frac{d\dot{p}_j}{dT} = \dot{T} - \frac{\dot{\xi}_j}{\dot{\xi}_i} \dot{p}_i
\]

\[
\frac{ds}{dT} = \frac{s^2}{\alpha} \quad \frac{d\xi_j}{dT} = \frac{1}{\alpha} \left[ -s^2 \dot{\eta}_j - gk_i \right] - s\dot{s}^2
\]

(Time scaled, "non canonical transformation")

\[\underline{\text{Nose-Hoover}}\]

Start w/ Nose &

\[
p_i = p_i'/s \quad \frac{dT}{ds} = dT'/s \quad \frac{1}{1} \frac{ds}{dT} = \frac{d\eta}{dT} \quad \frac{d\xi_j}{dT} = \frac{\dot{\eta}_j}{\dot{\eta}_i} \quad \frac{d\xi_j}{dT} = \frac{1}{\alpha} \left[ -s^2 \dot{\eta}_j - gk_i \right] - s\dot{s}^2
\]

(\( \eta \) from Martyna, 1992)

A Non- Energetic for Simple harmonic oscillator