Canonical sampling with MD

We said Hamiton's equations $\Rightarrow (N, V, \mathcal{E})$

want is sampling from $\underline{(N, V, T)}$ or $\underline{(N, P, T)}$

In MD microcanonical partition function

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

States $P(X) \propto \dfrac{1}{\Omega(N, V, \mathcal{E})}$

Goal: MD simulation, modified

$$P(\underline{X}) \propto e^{-\beta \mathcal{H}(x)} \qquad \underline{X} = (\vec{q}, \vec{p})$$

$$Z(N, V, T) = \int d\vec{q}\, d\vec{p}\; e^{-\beta \mathcal{H}(\vec{q}, \vec{p})}$$

or ok with

$$P(\underline{X}) = P(\vec{q}) \propto e^{-\beta U(\vec{q})}$$

Overall goal: averages

$$\langle A \rangle = \int dX\, A(x)\, e^{-\beta \mathcal{H}(X)}$$

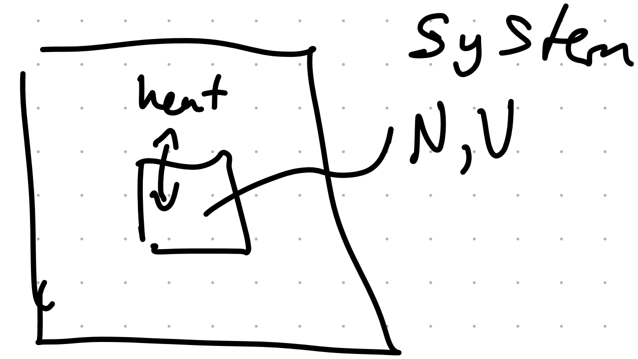
$$= C \int d\vec{q}\, A(\vec{q})\, e^{-\beta U(q)}$$

if $A(\vec{q}, \vec{p}) = A(\vec{q})$

Simple ways (not necessarily good)

1) T rescaling

keep making the temperature $= T$



$$\left.\begin{aligned}\left\langle \frac{1}{2} m v^2 \right\rangle &= \frac{3}{2} k_B T \\ \left\langle \sum_{i=1}^{N} \frac{1}{2} m_i v_i^2 \right\rangle &= \frac{3}{2} N k_B T\end{aligned}\right\} \text{ideal}$$

calculate this

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

$$\frac{V_{current}}{V_{ideal}} = \sqrt{\frac{T_{current}}{T_{ideal}}}$$

$$\Rightarrow \quad V_{new} = V_{current} \cdot \sqrt{\frac{T_{ideal}}{T_{current}}}$$

$Var(\mathcal{E}) \propto C_v$

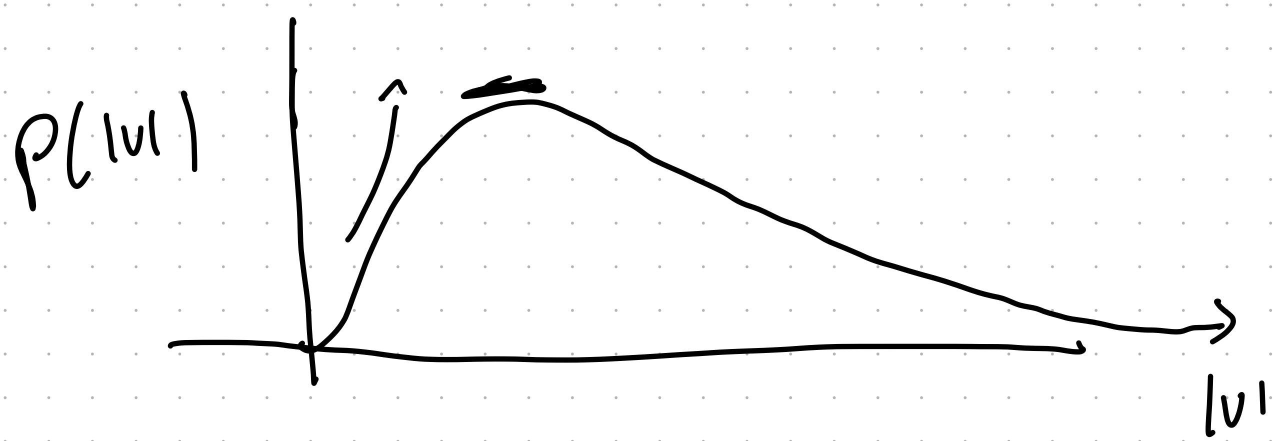
recaaling every time step $Var(KE) = 0$

2) Resample all velocities from a maxwell-boltzmann distribution

$P(\mathcal{E}) = e^{-\beta \mathcal{E}}$

$P(\frac{1}{2}mv^2) \propto e^{-\beta \frac{1}{2} m v^2}$

$P(|v|) \propto v^2 e^{-\beta \frac{1}{2} m v^2}$



Canonical momentum distribution, loses inertia

3) Reset a subset of the velocities, "p"
with frequency "f"

≈ pick 20% atoms every 100 timesteps (Δt)

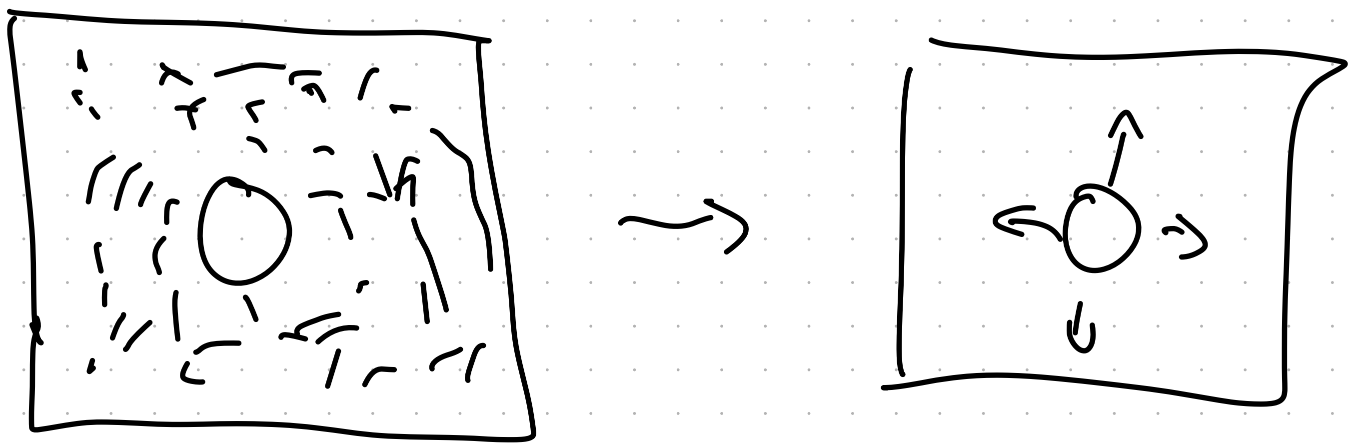
reset their velocities from M-B distribution
with a probability

random # < $f\Delta t$ then resample ≈

(Andersen)

⇒ good canonical sampling

Big idea 2 Langevin Dynamics inspired by Brownian Motion



Looks like rand forces and drag

$$F_i(X) = -\nabla U(X) - \gamma v(t) + \overset{\text{random}}{F_i(X, t)}$$

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

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

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

random forces give rise to correct "temperature"
canonical sampling of x

$$\underbrace{\langle F(t) F(t') \rangle}_{Var(F)} = 2\gamma k_B T \times \delta(t-t')$$

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

$$Var(A) = \langle (A - \langle A \rangle)^2 \rangle$$

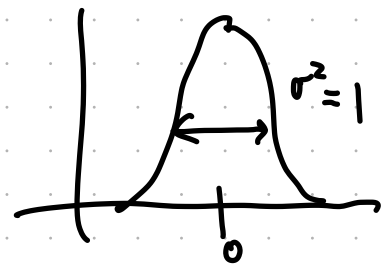
$$Var(F^{random}) = \langle (F^{rand} - \underset{\substack{\uparrow \\ 0}}{\langle F^{rand} \rangle})^2 \rangle = \langle F^{rand\,2} \rangle$$

$\langle A(t) B(0) \rangle = ?$ $\quad \langle F^{random}(t) B(t') \rangle = \begin{cases} 0 \text{ except} \\ B(t') = F^{random}(t) \end{cases}$

In practice

$$\frac{dq}{dt} = v$$

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



$R(t)$ is a random # sampled from $N(0,1)$

One limit of Langevin Dynamics is Brownian Dynamics

"overdamped" Langevin $\gamma \to \infty$

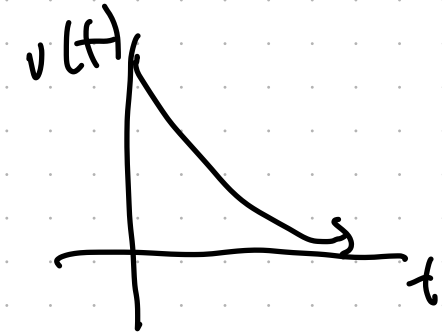
$$m \frac{dv}{dt} = -\nabla U - \gamma v + F^{random}(t) \qquad \leftarrow \text{LD}$$

consider LD w/o random force

$$m \frac{dv}{dt} = -\nabla U - \gamma v \xrightarrow[\gamma \to \infty]{} \approx -\gamma v$$

$$\frac{1}{v}\frac{dv}{dt} \approx -\frac{\gamma}{m} \Rightarrow v(t) = v(0)\, e^{-(\gamma/m)t}$$

$$\gamma/m \sim 1/\tau$$



$$m\frac{dv}{dt} = -\nabla U - v\gamma + F^{random}(t)$$

≈ 0

in $\gamma \to \infty$ limit $\quad v \approx 0 \quad \frac{dv}{dt} \approx 0$

$$0 = -\nabla U - \gamma v + F^{random}(t)$$

$$\frac{dq}{dt} = v(t) = -\frac{\nabla U}{\gamma} + \frac{F^{random}}{\gamma}(t)$$

$$dq = \left(-\frac{\nabla U}{\gamma} + \frac{F^{random}}{\gamma}\right)dt$$

easy to simulate

$$q(t+\Delta t) = q(t) + \left(-\frac{\nabla U}{\gamma} + \frac{F^{random}}{\gamma}\right)\Delta t$$

Last idea

Microcanonical sampling but for a modified $\mathcal{H}$ which has extra variables

if we simulate with $\mathcal{H}$ conserve E

with $\tilde{\mathcal{H}}$ conserve some other $\tilde{E}$

$\tilde{\mathcal{H}} = \mathcal{H} + V$ but

$\mathcal{H}(t)$ will fluctuate and $\langle \mathcal{H} \rangle = E$

Nosé (1983, 1984) idea is same

extra variable measures if KE is above or below the desired value, rescales KE

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

System depends on $3N$ q's, $3N$ p's, s, p_s

Q "mass" units of $[E][t^2]$, determines how fast rescaling happens (High Q, fast)

Sampling

$$\Omega_N = \int d\vec{q}^{\,N} \int d\vec{p}'^{\,N} \int ds \int dp_s \; \delta(\mathcal{H}(\vec{p}', \vec{q}, s, p_s) - \mathcal{E})$$

define $p_i = p_i'/s$

$$= \int d\vec{q}^{\,N} \int d\vec{p}^{\,N} \int ds \int dp_s \cdot s^{dN} \; \delta\Big(\mathcal{H}_{phys}(p,q) + \underbrace{\frac{p_s^2}{2Q} + g k_B T \ln s}_{} - \mathcal{E}\Big)$$

$$\mathcal{H}_{phys} = \sum p_i^2/2m + U(q)$$

... result is

$$\Omega = \int d\vec{p} \int d\vec{q} \int dp_s \, \frac{1}{g k_B T} \, e^{\frac{dN+1}{g k_B T}\left[\mathcal{E} - H - p_s^2/2Q\right]}$$

$$\int = \sqrt{\frac{2\pi Q}{\beta}}$$

$$g \equiv dN+1$$

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

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

Hamilton's Equation

$$\begin{cases} \dfrac{dp}{dt} = -\dfrac{\partial H}{dq} \\[2ex] \dfrac{dq}{dt} = \dfrac{\partial \mathcal{H}}{\partial p} \end{cases}$$

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

$$\frac{ds}{dt} = \frac{\partial \mathcal{H}}{\partial p_s} = \frac{p_s}{Q} \qquad \frac{dp_s}{dt} = -\frac{\partial \mathcal{H}}{\partial s}$$

$$\frac{dp_s}{dt} = -\frac{\partial \mathcal{H}}{\partial s} = \sum_{i=1}^{N} \frac{p_i'^2}{ms^3} - g\frac{k_B T}{s}$$

$$= \frac{1}{s}\left[\sum p_i'^2/ms^2 - g k_B T\right]$$

p_s Changes based on if $\sum_{i=1}^{N} \frac{p_i^2}{m} \sim 2KE$

bigger or smaller $(dN+1)k_B T$

expect $\frac{dN}{2} k_B T$ for KE

In practice:

Nosé – Hoover extension
better properties

Non-ergodic for S.H.O.

$\langle A \rangle_{\text{canonical}}$ many NVE simulations
starting X, E sampled from
N, V, T

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