Lecture 10 - Canonical Sampling

First, finish MD, microcanonical sampling

Idea: Have $U(x)$, $F = -\nabla u = ma$

$$a = \frac{d^2x}{dt^2} = -\frac{\nabla u}{m}$$

Do by taylor expansion

① $q(t+\Delta t) \approx q(t) + \Delta t\, v(t) + \frac{1}{2}\Delta t^2\, a(t)$

could also do

② $q(t-\Delta t) \approx q(t) - \Delta t\, v(t) + \frac{1}{2}\Delta t^2\, a(t)$

add $q(t+\Delta t) = 2q(t) - q(t-\Delta t) + (\Delta t)^2\, a(t)$

store current & previous position, compute $a(t)$

compute $v(t) = \frac{q(t+\Delta t) + q(t-\Delta t)}{2\Delta t}$ if needed

This is Verlet algorithm (1967)

Can get another scheme by considering revers.

$q(t+\Delta t) \to q(t)$

$$q(t+\Delta t) \approx q(t) - \Delta t\, v(t+\Delta t) + \frac{\Delta t^2}{2} a(t+\Delta t)$$

before

$$q(t+\Delta t) \approx q(t) + v(t)\Delta t + \frac{\Delta t^2}{2} a(t)$$

combining

$$v(t+\Delta t) = v(t) + \frac{1}{2}\Delta t \left[a(t) + a(t+\Delta t) \right]$$

Now alternate these, 'velocity verlet'
store q & v

We easily arrive at this algorithm from our formal results last time

[See Tuckerman 3.8]

said $A(t) = e^{i\mathcal{L}t} A(0)$

where $-i\mathcal{L}A = \{\mathcal{H}, A\}$

$$= \sum_{i=1}^{N} \frac{\partial \mathcal{H}}{\partial q_i}\frac{\partial A}{\partial p_i} - \frac{\partial \mathcal{H}}{\partial p_i}\frac{\partial A}{\partial q_i}$$

Ski Sec 3.10.

Lets work for 1 particle in 1d for simplicity

$$\mathcal{L} = \mathcal{L}_p + \mathcal{L}_q$$

$$i\mathcal{L}_p = -\frac{\partial \mathcal{H}}{\partial q}\frac{\partial}{\partial p} \qquad i\mathcal{L}_q = \frac{\partial \mathcal{H}}{\partial p}\frac{\partial}{\partial q}$$

If $\mathcal{H} = \frac{p^2}{2m} + U(q)$

$$i\mathcal{L}_p = F\cdot\frac{\partial}{\partial p} \qquad i\mathcal{L}_q = \frac{p}{m}\frac{\partial}{\partial q} = v\frac{\partial}{\partial q}$$

$$= \frac{F}{m}\cdot\frac{\partial}{\partial v} = a\frac{\partial}{\partial v}$$

Trotter so $e^{i\mathcal{L}t} \approx \left[e^{i\mathcal{L}_p \frac{t}{2p}} e^{i\mathcal{L}_q \frac{t}{p}} e^{i\mathcal{L}_p \frac{t}{2p}} \right]^p + O(p\Delta t^3)$

$O(t\Delta t^2)$

[one splitting] let $t/p = \Delta t$

$$\approx \left[e^{a\frac{\Delta t}{2}\frac{\partial}{\partial v}} e^{v\Delta t\frac{\partial}{\partial q}} e^{a\frac{\Delta t}{2}\frac{\partial}{\partial v}} \right]^p$$

$$e^{i\mathcal{L}t} \approx \left[e^{a\frac{\Delta t}{2}\frac{\partial}{\partial v}} e^{v\Delta t\frac{\partial}{\partial q}} e^{a\frac{\Delta t}{2}\frac{\partial}{\partial v}} \right]^{P}$$

$$e^{i\mathcal{L}t} \begin{bmatrix} q(0) \\ v(0) \end{bmatrix} = ?$$ apply right to left

$$e^{c\frac{\partial}{\partial x}} g(x) = g(x+c)$$ why?

$$e^{c\frac{\partial}{\partial x}} = 1 + c\frac{\partial}{\partial x} + \frac{1}{2}c^2\frac{\partial^2}{\partial x^2} + \cdots$$

$$g(x+c) \approx g(x) + c\frac{dg(x)}{dx} + \frac{1}{2}c^2\frac{d^2g}{\partial x^2} + \cdots$$

So: 1 step

$$e^{a\Delta t/2\,\frac{\partial}{\partial v}} \begin{bmatrix} q(0) \\ v(0) \end{bmatrix} = \begin{bmatrix} q(0) \\ v(0) + a\frac{\Delta t}{2} \end{bmatrix}$$

$$e^{v\Delta t\,\partial/\partial q} \begin{bmatrix} \ \\ \ \end{bmatrix} = \begin{bmatrix} q(0) + \Delta t\left[v(0) + a(0)\frac{\Delta t}{2}\right] \\ v(0) + a(0)\frac{\Delta t}{2} \end{bmatrix}$$

$$e^{a\frac{\Delta t}{2}\frac{\partial}{\partial v}} \begin{bmatrix} \ \\ \ \end{bmatrix} = \begin{bmatrix} q(0) + \Delta t\left[v(0) + a(0)\frac{\Delta t}{2}\right] \\ v(0) + a(0)\frac{\Delta t}{2} + a(1)\frac{\Delta t}{2} \end{bmatrix}$$

Can let us derive more interesting schemes

This all gives microcanonical sampling
How can we get canonical?

Want schemes where samples either come from $e^{-\beta \mathcal{H}(q,p)}$ or $e^{-\beta U(q)}$

Simple approaches:

1) T - rescaling

$$P(v) = e^{-\beta \cdot \frac{1}{2} m v^2} \Big/ \sqrt{2\pi m k_B T}$$ for each dof

$$\langle v^2 \rangle = \frac{k_B T}{m} \Rightarrow \langle \tfrac{1}{2} m v^2 \rangle = \frac{k_B T}{2}$$

so can calculate $\langle \frac{1}{2} m v^2 \rangle = \frac{k_B T_{current}}{2}$

and compare to $\langle \frac{1}{2} m v_{ideal}^2 \rangle = \frac{k_B T_{ideal}}{2}$

$$\Rightarrow v_{ideal} = \sqrt{\frac{T}{T_{current}}} \cdot v_{current}$$

Do periodically

(2) Sample v's from Boltzmann distribution

Lose inertia! But full v-distribution is correct, not just mean

(3) Do this, but just for a single particle randomly, as if colliding with bath

Andersen thermostat

Better schemes:

Langevin Dynamics:

Apply random forces as if there is a temp bath

Later in sem

Other good idea: $\left[\dot{p} = -\frac{\partial H}{\partial q} \quad \dot{q} = \frac{\partial H}{\partial p}\right]$

Microcanonical sampling but for a different, "extended" ensemble.

Nosé [1983, 1984], checks if KE ~~too~~ high or low & continuously rescales velocities

$$H_N = \sum_{i=1}^{N} \tilde{p}_i^2 / 2ms^2 + U(q) + \frac{p_s^2}{2Q} + g k_B T \ln s$$

rescales

KE of s

fake mass

pot on s

Q: determines timescale of rescaling
units $[E][t^2]$

why? $[p_s^2]/[Q] = [E]$

$[Q] = [p_s^2]/[E]$

$[\dot{p}_s] = \left[\frac{\partial H}{\partial s}\right] = [E]$

so $[p_s] = [E][t]$

$2dN+2$ dimensions, s always positive

have to find g to give canonical

also, real $p = p'/s$

$$\Omega_N(N,V,\mathcal{E}) = \int dq^{dN} \int dp'^{dN} \int ds \int dp \qquad \int dp^{dN} s^{dN}$$

$$\delta\Big(\underbrace{\mathcal{H}_{phys}(p,q) + \frac{p_s^2}{2Q} + g k_B T \ln s - \mathcal{E}}_{f(s)}\Big)$$

[Tuckerman 4.8]

where is $f(s_0) = 0$?

$$g k_B T \ln s_0 = \mathcal{E} - \mathcal{H} - \frac{p_s^2}{2Q}$$

$$s_0 = e^{-\frac{1}{g k_B T}\left[H + p_s^2/2Q - \mathcal{E}\right]}$$

$$\delta(f(s)) = \delta(s - s_0) \Big/ \left| \frac{df}{ds}\Big|_{s_0} \right|$$

$$\left.\frac{df}{ds}\right|_{s_0} = \left.\frac{g k_B T}{s}\right|_{s_0} = \frac{g k_B T}{s_0}$$

$$= g k_B T \, e^{+\frac{1}{g k_B T}\left(H + p_s^2/2Q - \varepsilon\right)}$$

$$\Omega = \int dp^{dN} \int dq^{dN} \int ds \int dp_s \, s^{dN}$$

$$\frac{\delta(s - s_0)}{g k_B T} \, e^{-\frac{1}{g k_B T}\left[H + p_s^2/2Q - \varepsilon\right]}$$

$$= \int dp^{dN} \int dq^{dN} \int dp_s \cdot \frac{1}{g k_B T} \cdot e^{-\frac{(dN+1)}{g k_B T}[\;]}$$

Now, let $g = dN+1$

$$\Omega = \int dp^{dN} \int dq^{dN} \int dp_s \frac{1}{(dN+1)k_BT} e^{\beta E} e^{-\beta H} e^{-\beta p_s^2/2Q}$$

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

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

What are the dynamics?

$$\dot{q}_i = \frac{d\mathcal{H}_\sim}{\partial \tilde{p}_i} = \frac{\tilde{p}_i}{m_i s^2}$$

$$\dot{\tilde{p}}_i = -\frac{d\mathcal{H}_\sim}{dq_i} = -\frac{\partial U}{\partial q_i} = F_i$$

$$\dot{s} = \frac{\partial \mathcal{H}}{\partial p_s} = p_s / Q$$

$$\dot{p}_s = -\frac{\partial \mathcal{H}}{\partial s} = \sum \frac{\tilde{p}_i^2}{m s^3} - g\frac{k_B T}{s}$$

$$= \frac{1}{s}\left[\sum \frac{\tilde{p}_i^2}{m s^2} - g k_B T\right]$$

P_S changes if $2\times$

KE bigger or smaller

than $(2dN+1)k_BT$

Nose-Hoover, doesn't

need time transform,

but non-ergodic for

S.H.O.