Lecture 9 - Classical Mechanics to MD simulations

Last time:

$$\langle O \rangle = \int d\vec{X}\, P(\vec{X})\, O(\vec{x})$$

Do this by generating trajectory

$$\vec{X}_1 \to \vec{x}_2 \to \dots \to \vec{x}_N$$

$\vec{X} \sim P(\vec{X})$
(sampled from)

$$\langle O \rangle = \frac{1}{N} \sum_{i=1}^{N} O(\vec{x}_i)$$

Classical Mechanics

$\vec{x} = (\vec{x}_1, \ldots, \vec{x}_N)$

$\vec{v} = (\vec{v}_1, \ldots, \vec{v}_N)$

3D

$$\vec{v} = \frac{d\vec{x}}{dt} = \dot{\vec{x}}$$

$$\vec{a} = \frac{d\vec{v}}{dt} = \frac{d^2\vec{x}}{dt^2} = \ddot{\vec{x}}$$

Newton's Equations

$m_i \ddot{x}_i = F_i(\vec{x})$ 3N diff eqns

if we know $\vec{x}(0)$ & $\vec{v}(0)$

then we know @ all t

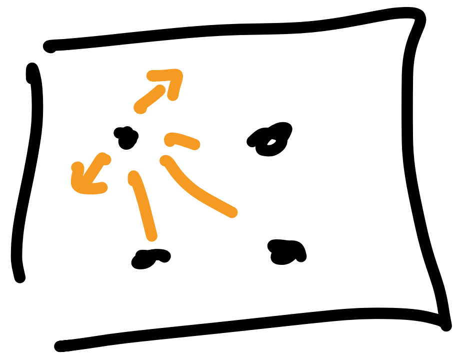
If no friction, know $U(\vec{x})$

$$F(\vec{x}) = -\nabla U(\vec{x})$$

conservative force

$$\nabla = \left(\frac{\partial}{\partial \vec{x}_1}, \frac{\partial}{\partial \vec{x}_2}, \dots, \frac{\partial}{\partial \vec{x}_N}\right)$$

$$m\ddot{x}_i = -\frac{\partial U(\vec{x})}{\partial x_i}$$



Total energy

$$\mathcal{E}(\vec{x}, \vec{v}) = \sum_{i=1}^{N} \frac{1}{2} m_i \vec{v}_i^{\,2} + U(\vec{x})$$

$$[\vec{p}_i = m_i \vec{v}_i]$$

$$\mathcal{E}(\vec{x},\vec{v}) = \sum_{i=1}^{N} \frac{1}{2} m_i \vec{v}_i^{\,2} + U(\vec{x})$$

$$\vec{x} = \{x_1, x_2, \ldots, x_N\}$$

$$\frac{d\mathcal{E}}{dt} = \sum_{i=1}^{N} \Big[\underline{m_i}\, \overbrace{v_i \underline{\frac{d\vec{v}_i}{dt}}}^{F_i} \Big] + \sum_{i=1}^{N} \underbrace{\left(\frac{\partial U}{\partial \vec{x}_i}\right)}_{-F_i} \underbrace{\left(\frac{\partial \vec{x}_i}{dt}\right)}_{v_i}$$

$$\frac{d\,(v^2)}{dt} = 2v \frac{dv}{dt}$$

$$= \sum_{i=1}^{N} \vec{F}_i \vec{v}_i \qquad \sum_{i=1}^{N} -\vec{F}_i \vec{v}_i \qquad = 0$$

Lagrangian Mechanics

[Sec 1.6]

$$\mathcal{L}(\vec{q}, \dot{\vec{q}}) = K(\dot{\vec{q}}) - U(\vec{q})$$

Euler - Lagrange Eqns

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{q}_i}\right) - \frac{\partial \mathcal{L}}{\partial \vec{q}_i} = 0$$

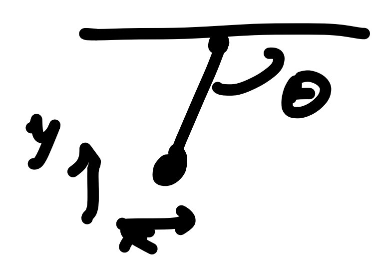
3N diff Eqns

î $K = \frac{1}{2} m \dot{q}^2$

$$m \ddot{q}_i = -\frac{\partial U}{\partial q_i}$$

← same as newtonian

q doesn't have to be cartesian $q_i = f_i(\vec{x})$



Hamiltonian Mechanics

$$\mathcal{H}(\vec{q}, \vec{p}) \qquad p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i}$$

$$\left[K(\dot{q}) = \frac{1}{2} m \dot{q}_i^2 \quad p_i = m_i \dot{q}_i \right]$$

$$\mathcal{L}(\vec{q}, \dot{\vec{q}}) = K(\dot{\vec{q}}) - U(\vec{q})$$

Legendre transform

$$\mathcal{H} = \left[\mathcal{L}(\vec{q}, \dot{\vec{q}}) - \dot{\vec{q}} \, \underbrace{\frac{\partial \mathcal{L}}{\partial \dot{\vec{q}}}}_{``\vec{p}_i"} \right] \cdot -1$$

$$\mathcal{H}(\vec{q}, \vec{p}) = \dot{q}_i p_i - \mathcal{L}$$

$$\mathcal{H} = \sum_{i=1}^{N} \frac{\partial \mathcal{L}}{\partial \dot{q}_i} \dot{q}_i - \mathcal{L}$$

$\left[H = \frac{P^2}{2m} + \frac{1}{2} k q^2 \right.$

$\mathcal{L} = K - \mathcal{U}$ $\qquad K = \frac{1}{2} m \dot{q}_i^2$

$= U + KE$ (total energy for cartesian)

$\mathcal{H}$ generates dynamics arbitrary coord

$$\boxed{\begin{aligned} \dot{\vec{q}}_i &= \partial \mathcal{H} / \partial \vec{p}_i \\ \dot{\vec{p}}_i &= -\partial \mathcal{H} / \partial \vec{q}_i \end{aligned}}$$

Hamilton's Eqns

$$\mathcal{H} = \frac{p^2}{2m} + \frac{1}{2} k q^2$$

Harmonic Oscillator

$$F = -kq \quad \left[-\frac{\partial \mathcal{H}}{\partial q} \right]$$

$$\frac{\partial \mathcal{H}}{\partial p} = p/m = \text{velocity} = \dot{q}$$

$$\left[\begin{array}{l} p = mv \\ \dot{p} = ma = F \end{array} \right.$$

$$\frac{\partial \mathcal{H}}{\partial q} = kq = -F = -\dot{p}$$

$\mathcal{H}$ is conserved by Hamilton's Eqn

$\mathcal{H}(\vec{q}, \vec{p})$

$$\frac{d\mathcal{H}}{dt} = \sum_{i=1}^{N} \left(\frac{\partial \mathcal{H}}{\partial q_i}\right) \frac{\partial q_i}{\partial t} + \frac{\partial \mathcal{H}}{\partial p_i} \frac{\partial p_i}{\partial t}$$

$$-\dot{p}_i \quad \dot{q}_i \quad + \quad \dot{q}_i \quad \dot{p}_i \qquad = 0$$

Phase space:

$$\vec{X} = \{\vec{q}_1, \vec{q}_2, \ldots \vec{q}_N, \vec{P}_1, \vec{P}_2, \ldots, \vec{P}_N\}$$

$$\frac{d}{dt}a(\vec{x}) = \sum_{i=1}^{N}\left(\frac{\partial a}{\partial \vec{q}_i}\right)\left(\frac{\partial q_i}{\partial t}\right) + \left(\frac{\partial a}{\partial \vec{p}_i}\right)\left(\frac{\partial p_i}{\partial t}\right)$$

$$\dot{q}_i = \frac{\partial H}{\partial p_i} \qquad \dot{p}_i = -\frac{\partial H}{\partial q_i}$$

$$= \sum_{i=1}^{N}\left(\frac{\partial a}{\partial \vec{q}_i}\right)\left(\frac{\partial H}{\partial \vec{p}_i}\right) - \left(\frac{\partial a}{\partial \vec{p}_i}\right)\left(\frac{\partial H}{\partial \vec{q}_i}\right)$$

Define Poisson Bracket

$$\{a, b\} = \sum_{i=1}^{N}\left(\frac{\partial a}{\partial q_i}\frac{\partial b}{\partial p_i}\right) - \left(\frac{\partial a}{\partial p_i}\right)\left(\frac{\partial b}{\partial q_i}\right)$$

$$\frac{da}{dt} = \{a, H\}$$

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$$\{a,H\} = \sum_i \frac{\partial a}{\partial q}\frac{\partial H}{\partial p} - \frac{\partial a}{\partial p}\frac{\partial H}{\partial q}$$

Conserved quantity has

[Ch 2.5]

$$\frac{da}{dt} = 0, \quad \{a, H\} = 0$$

Eg is $\mathcal{H}$ itself

$$a(\vec{x}) = \sum_{j=1}^{N} \vec{p}_j \leftarrow$$

conservation law

$$\{a, \mathcal{H}\} = -\sum_{i=1}^{N} \frac{\partial \sum p_j}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i} = \sum -\frac{\partial H}{\partial q_i} = \sum_{i=1}^{N} F_i$$

"Molecular Dynamics"

$\{\vec{q}(0), \vec{p}(0)\} \rightarrow \{\vec{q}(t), \vec{p}(t)\}$

iteratively go from

$t \rightarrow t + \Delta t$

If the system is ergodic

then as $t \rightarrow \infty$

$\mathcal{H}$ is conserved

see every state w/ prob

$$P(\vec{q}\vec{p}) = \frac{1}{\Omega(N,V,E)}$$

If ergodic, are sampling from

N, V, E distribution

$$\langle O \rangle = \frac{1}{N} \sum_{i=1}^{N} O(x_i) \quad \leftarrow \text{time averages}$$

assume $\lim_{T \to \infty} \langle O \rangle_{time} = \langle O \rangle_{ensemble}$

$T = N \Delta T$

In practice: (1) Starting cfg $\vec{q}(0), \vec{p}(0)$

(2) interaction energy, $U(\vec{q})$

$$\vec{q}(t+\Delta t) \approx \vec{q}(t) + \Delta t \frac{dq}{dt} + \frac{1}{2}\Delta t^2 \frac{d^2q}{dt^2} + \cdots$$

$$x_2 - x_1 = tv + \frac{1}{2}at^2 \qquad \left(a = -\frac{\partial U}{\partial q}\right.$$

$$= tv + \frac{F}{2m}t^2$$

How get velocities

→ finite diff $\frac{dv}{dt} = \frac{q(2) - q(1)}{\Delta t}$

or → $v(t+\Delta t) = v(t) + \Delta t \cdot \frac{dv}{dt} + \cdots$

$$= v(t) + \Delta t \cdot \frac{F}{m}$$

Better: leapfrog, velocity verlet ..

More formal:

$$\frac{dA}{dt} = \{A, H\}$$

define $i\mathcal{L} = \{H, -\}$

$$\frac{dA}{dt} = -i\mathcal{L}A$$

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

$$\frac{dA}{dt} = -i\mathcal{L}\, e^{-i\mathcal{L}t} A(0) = -i\mathcal{L}A$$

$$i\mathcal{L} = i\mathcal{L}_1 + i\mathcal{L}_2$$

$$e^{A+B} \neq e^{A} e^{B}$$

Trotter factorization

$$e^{A+B} = \lim_{p\to\infty} \left[e^{A/2p} e^{B} e^{A/2p} \right]^{p}$$

it choose A & B correctly
gives you velocity verlet

$$e^{-i\mathcal{L}t} \vec{x} = \left[e^{A/2p} e^{B} e^{A/2p} \right] \cdots\cdots [\ ] \vec{x}$$