Lecture 9: Classical mechanics to Molecular Dynamics

Last time:

sample from dist $P(x)$
by generating Markov chain

$$x_1 \to x_2 \to \dots \to x_N$$

Monte Carlo gave us one way to do this

Said that MD is an alternative

Need to go deeper on classical mechanics to understand MD fully

Classical Mechanics

Assume our systems will be classical

$\vec{r} = (\vec{r}_1, \vec{r}_2, \dots \vec{r}_N)$

$\vec{v} = (\vec{v}_1, \vec{v}_2, \dots, \vec{v}_N)$

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

$\vec{a} = \dot{\vec{v}} = \ddot{\vec{r}}$

Newton's Equations say $F = ma$ ie

$m_i \ddot{r}_i = F_i(\vec{r}_1, \dots, \vec{r}_N)$, $3N$ diff eq

if we know $\vec{v}(0)$ and $\vec{r}(0)$, and $F(r)$,
everything is determined

If no friction, or dissipation, and know potential energy $U(\vec{r})$
then $F(\vec{r}) = -\nabla U(\vec{r})$ ie

$F_i(\vec{r}) = -dU(r)/dr_i$ (no dep on vel)

The total $\mathcal{E}$ is kinetic + pot energy

$\mathcal{E}(\vec{r}, \vec{v}) = \frac{1}{2} m \vec{v}^2 + U(r) = \vec{p}^2/2m + U(r)$

Momentum $p_i = v_i m_i$

If $F = -\nabla U$, say these are conservative forces because $\mathcal{E}$ is const

$\frac{d\mathcal{E}}{dt} = \frac{1}{2} m (v\dot{v} + \dot{v}v) + \frac{dU(r)}{dt}$

chain rule $\left[\frac{dX}{dt} = \sum_{i=1}^{N} \left(\frac{\partial X}{\partial l_i} \right) \frac{dl_i}{dt} = \sum \left(\frac{\partial X}{\partial t} \right) \dot{l}_i \right]$

$= \vec{m}\vec{v}\vec{a} + \sum \frac{\partial U}{\partial r_i} \dot{r}_1 = \vec{v} \cdot \vec{F} - \vec{F} \cdot \vec{v} = 0$

Lagrangian Mechanics

For conservative systems, there is another way to solve classical problems called Lagrangian Mechanics:

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

Euler-Lagrange equations:

$$\frac{d}{dt}\left(\frac{\partial \mathcal{L}}{\partial \dot{r}_i}\right) - \partial \mathcal{L}/\partial r_i = 0 \qquad \text{(Sec 1.6)}$$

For $\vec{K} = \frac{1}{2} m \dot{r}_i^2$, equiv to

$$m\ddot{r} = -\nabla U = F$$

Why is this helpful? It applies for other coordinates, ie where $q_i = f_i(\vec{r})$, could be diff func for each coord

Lagrangian Mech. is useful for some methods, but also leads to a second generalized set of EOMs, Ham. Mech.

$\mathcal{H}(\vec{r}, \vec{p})$ is Hamiltonian and $\vec{p}$ are "conj. mom."

In cartesian, $\vec{p} = \vec{m}\vec{v}$, but generalize to

$$p_i = \frac{\partial \mathcal{L}}{\partial \dot{q}_i} \quad \left[\text{Same for } K(\dot{q}) = m\dot{q}_i^2/2\right]$$

$$K = \sum p_i^2/2m_i, \quad \mathcal{H} = K + U(q)$$

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

$\mathcal{H}$ generates dynamics in any coord system

The $\mathcal{H}$ and $\mathcal{L}$ are connected by a "Legendre transform" [sec 1.5]

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

[for cartesian, $\sum m_i v_i^2 - \left(\frac{1}{2}\sum m_i v_i^2 - U\right) = U + K$]

$$\frac{dH(q,p)}{dt} = \sum \frac{\partial \mathcal{H}}{\partial q_i}\dot{q}_i + \frac{\partial \mathcal{H}}{\partial p_i}\dot{p}_i = \sum -\dot{p}_i\dot{q}_i + \dot{q}_i\dot{p}_i = 0$$

so, $\mathcal{H}$ is conserved .. [total $\mathcal{E}$ for cartesian]

Phase space is the coordinates describing everything about the system

so, $X(t) = \{q_1(t), q_2(t), \dots, q_{3N}(t), p_1(t), \dots p_{3N}(t)\}$

$\mathcal{H}(x)$ is one function of x, and we showed that $\frac{dH(x)}{dt} = 0$ if the system follows hamiltonian/newtonian dynamics

How do other quantities change with time? By the chain rule formula

$$d\,a(x)/dt = \sum_{i=1}^{3N}\left(\frac{\partial a}{\partial q_i}\frac{dq_i}{dt} + \frac{\partial a}{\partial p_i}\frac{dp_i}{dt}\right) = \sum_{i=1}^{3N} \frac{\partial a}{\partial q_i}\frac{\partial \mathcal{H}}{\partial p_i} - \frac{\partial a}{\partial p_i}\frac{\partial \mathcal{H}}{\partial q_i}$$

if we define $\{a,b\} \equiv \sum_{i=1}^{3N} \frac{\partial a}{\partial q_i}\frac{\partial b}{\partial p_i} - \frac{\partial a}{\partial p_i}\frac{\partial b}{\partial q_i}$ (Poisson Bracket)

then we see that $\boxed{\frac{da(x)}{\partial t} = \{a, H\}}$

A conserved quantity, one that doesn't depend on time, i.e.

$da/dt = 0$, e.g. we showed $\frac{dH}{dt} = 0$

so $\{H, H\} = 0$.

Another example, $a(\vec{X}) = \vec{P}_{tot} = \sum_{i=1}^{N} p_i$

$\frac{dP_i}{dt} = \{p_i, H\} = -\partial H/\partial q_i = F_i$

$d\vec{P}_{tot}/dt = \sum \vec{F}_i$, so if net force is 0, momentum is conserved

More advanced, phase space density & Liouville Eqn, Ch 2.5 ☆ [or past notes]

Molecular Dynamics Sims

$\Rightarrow$ Molecular dynamics is an alternative idea to solve classical equations approximately, with the same idea of computing $\langle O \rangle = \int dx\, P(x)\, O(x)$

We know from before, if we have $\{\vec{q}(0), \vec{p}(0)\}$ and $\mathcal{H}$, then we can generate $\{\vec{q}(t), \vec{p}(t)\}$ at any time t using $\vec{F} = m\ddot{\vec{q}}$, $\vec{F}_i = -\partial U / \partial \vec{q}_i$

or alternatively $\partial \mathcal{H} / \partial q_i = -\dot{p}_i \quad \partial \mathcal{H} / \partial p_i = \dot{q}_i$

If the system is "ergodic", then as $t \to \infty$ will sample all configurations $\{p(t), q(t)\}$ st $\mathcal{H}(p(t), q(t)) = E$

with equal prob, ie $P(\vec{X}) = P(\vec{p}, \vec{q}) = 1/\Omega(N, V, E)$

so $\langle O \rangle = C \int d\vec{p} \int d\vec{q}\; O(p,q)\, \delta(\mathcal{H}(p,q) - E) / \Omega(N,V,E)$

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

& if ergodic $\langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T dt\, A[p(t), q(t)]$

In practice, need: 1) initial starting cfg (gen vel from Boltzmann dist)
2) interaction energy

Remember we previously said $\frac{dA}{dt} = \{A,H\} = \sum_{i=1}^{N}\left(\frac{\partial A}{\partial q_i}\underbrace{\frac{dq_i}{dt}}_{= \partial H/\partial p_i} + \frac{\partial A}{\partial p_i}\underbrace{\frac{dp_i}{dt}}_{= -\partial H/\partial q_i}\right)$

We can define $i\mathcal{L}A = \{H, A\}$, $i\mathcal{L} = \{H, \_\}$

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

formally $A(t) = e^{-i\mathcal{L}t}A(0)$, but we cannot solve this for almost any problem, and so we can use a computer to solve these equations approximately

First, look at the way we can do this by looking at Newtonian dynamics as a taylor series in position at small time

(1) $$\vec{q}(\tau + d\tau) \approx \vec{q}(\tau) + d\tau \left.\frac{d\vec{q}}{dt}\right|_{t=\tau} + \frac{d\tau^2}{2}\left.\frac{d^2\vec{q}}{dt^2}\right|_{t=\tau} + O(d\tau^3)$$

$$\approx \vec{q}(\tau) + d\tau\,\vec{v}(\tau) + d\tau^2/_2\,\vec{a}(t)$$ [Remember: $d = vt + \frac{1}{2}at$

Remember $a_i(t) = -\frac{\partial U(q(t))}{\partial q_i}\cdot\frac{1}{m_i} \doteq F_i/m$

Also would need $v(\tau + d\tau)$, can do by finite diff

[$\vec{v} = d\vec{q}/d\tau \approx \frac{\vec{q}(t+d\tau) - \vec{q}(t)}{d\tau}$] or by expanding

$\vec{v}(t + d\tau) \approx \vec{v}(t) + d\tau\,\vec{a}(t) + O(d\tau^2)$, but people came up with schemes that are better.

Lets go back to formal description

$$dP/dt = -\frac{\partial H}{\partial q} \qquad \frac{dq}{dt} = \frac{\partial H}{\partial p}$$

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

$$dA/dt = \{A, H\} \Rightarrow A(t) = e^{+i\mathcal{L}t} A(0),$$

Schemes to split $i\mathcal{L}t$

Now, $e^{A+B} \neq e^{A}e^{B}$ unless $[A, B] = AB - BA = 0$
and can show that $[+i\mathcal{L}_p, +i\mathcal{L}_q] \neq 0$, don't commute

however
Trotter Factorization $\quad e^{A+B} = \lim_{P\to\infty}\left[e^{A/2P}\, e^{B/P}\, e^{A/2P}\right]^{P}$