Lecture 9: Classical mechanics to Molecular Dynamics

Last time,
Sample from dist Plx) by generating Markov chain
$x_1 \rightarrow x_2 \rightarrow \ldots \rightarrow x_N$
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

\[ \mathbf{F} = (F_1, F_2, \ldots, F_n) \]
\[ \mathbf{V} = (V_1, V_2, \ldots, V_n) \]
\[ \mathbf{a} = \frac{d\mathbf{V}}{dt} = \frac{d^2 \mathbf{r}}{dt^2} \]
\[ \mathbf{\ddot{r}} = \mathbf{\dot{a}} = \mathbf{\ddot{r}} \]

Newton's Equations say \( \mathbf{F} = m\mathbf{a} \) i.e.

\[ m_i \mathbf{\ddot{r}}_i = \mathbf{F}_i (\mathbf{r}_1, \ldots, \mathbf{r}_n) \], 3N diff eq

If we know \( \mathbf{V}(t) \) and \( \mathbf{r}(t) \), and \( \mathbf{F}(t) \), every thing is determined

If no friction, or dissipation, and know potential energy \( U(\mathbf{r}) \)

then \( \mathbf{F}(\mathbf{r}) = -\nabla U(\mathbf{r}) \) i.e

\[ \mathbf{F}_i(\mathbf{r}) = -\frac{\partial U(r)}{\partial r_i} \] (no dep on vel)

The total \( E \) is kinetic + pot energy

\[ E(\mathbf{r}, \mathbf{V}) = \frac{1}{2} m \mathbf{V}^2 + U(\mathbf{r}) = \frac{\mathbf{r}^2}{2m} + U(\mathbf{r}) \]

Momentum \( \mathbf{p}_i = \mathbf{v}_i m_i \)

If \( \mathbf{F} = -\nabla U \), say these are conservative forces because \( E \) is cons

\[ \frac{dE}{dt} = \frac{1}{2} m (\mathbf{v}_i + \mathbf{v}_i) + \frac{du(r)}{dt} \]

chain rule

\[ \left[ \frac{dx}{dt} = \sum_{i=1}^{n} \left( \frac{\partial x}{\partial \mathbf{l}_i} \right) \frac{d\mathbf{l}_i}{dt} = \sum \left( \frac{\partial x}{\partial \mathbf{r}_i} \right) \mathbf{\dot{r}}_i \right] \]

\[ = m \mathbf{V} \mathbf{a} + \sum \frac{\partial u}{\partial \mathbf{r}_i} \mathbf{\dot{r}}_i = \mathbf{V} \cdot \mathbf{F} - \mathbf{F} \cdot \mathbf{V} = 0 \]
Lagrangian Mechanics

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

\[ L(q, \dot{q}) = K(q) - U(q) \]

Euler-Lagrange equations:

\[ \frac{d}{dt} \left( \frac{\partial L}{\partial \dot{q}_i} \right) - \frac{\partial L}{\partial q_i} = 0 \quad (\text{Sec 1.6}) \]

For \( p_i = \frac{1}{2} m_i \dot{q}_i^2 \), equiv to

\[ m \ddot{q}_i = -\nabla U = F \]

Why is this helpful? It applies for other coordinates, i.e. where \( q_i = f_i(r) \), 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.

\[ H(p_i, q_i) \] is Hamiltonian and \( p_i \) are "conj. mom." In cartesian, \( p_i = m \dot{q}_i \), but generalize to

\[ p_i = \frac{\partial H}{\partial \dot{q}_i} \quad \text{[Same for } K(q) = \frac{1}{2} m \dot{q}^2 \text{]} \]

\[ H = \sum p_i \dot{q}_i \quad K + U(q) \]

\( H \) generates dynamics in any coord system.

The \( H \) and \( L \) are connected by a "Legendre transform" [Sec 1.5]

\[ H(p_i, q_i) = \sum \frac{\partial L}{\partial \dot{q}_i} \dot{q}_i - L = \sum p_i \dot{q}_i - L \quad \text{[for cart. \( \sum m_i \dot{q}_i^2 - \frac{1}{2} \sum m_i \dot{q}_i^2 = 0 \)]} \]

\[ \dot{q}_i = \frac{\partial H}{\partial p_i}; \quad \dot{p}_i = - \frac{\partial H}{\partial q_i} \]

\[ \frac{d}{dt} \left( \sum q_i \dot{q}_i \right) = \sum \frac{\partial H}{\partial q_i} \dot{q}_i + \frac{\partial H}{\partial \dot{q}_i} \ddot{q}_i = \sum -\dot{q}_i \dot{q}_i + \ddot{q}_i \dot{p}_i = 0 \]
so, $\mathcal{H}$ is conserved - \text{[total $E$ for cartesian]}

Phase space is the coordinates describing everything about the system
SO, $X(t) = [q_1(t), q_2(t), \ldots, q_n(t), p_1(t), p_2(t), \ldots, p_n(t)]$
$H(x)$ 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

\[
\frac{d\alpha(x)}{dt} = \sum_{i=1}^{\infty} \left( \frac{\partial \alpha}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial \alpha}{\partial p_i} \frac{dp_i}{dt} \right) = \sum_{i=1}^{\infty} \left( \frac{\partial \alpha}{\partial q_i} \frac{dq_i}{dt} - \frac{\partial \alpha}{\partial p_i} \frac{dp_i}{dt} \right)
\]

If we define $\Xi_{a,b} = \sum_{i=1}^{\infty} \left( \frac{\partial a}{\partial q_i} \frac{\partial b}{\partial q_i} - \frac{\partial a}{\partial p_i} \frac{\partial b}{\partial p_i} \right)$ (Poisson Bracket)

then we see that $\frac{d\alpha(x)}{dt} = \Xi_{a,H}$

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

\[
\frac{d\alpha}{dt} = 0, \text{ e.g. we showed } \frac{dH}{dt} = 0
\]

so $\sum H, H_3 = 0$.

Another example, $\alpha(X) = P_{tot} = \sum p_i$

\[
\frac{dp_i}{dt} = \Xi_{p_i, H_3} = -\frac{\partial H}{\partial q_i} = F_i
\]

\[
\frac{d^2p_i}{dt^2} = \sum F_i, \text{ so if net force is 0, momentum is conserved}
\]

More advanced, phase space density & Lioville Eqn, ch 2.5 & [or past notes]
Molecular Dynamics Sims

Molecular dynamics is an alternative idea to solve classical equations approximately, with the same idea of computing \( \langle \mathcal{O} \rangle = \int dx \rho(x) \mathcal{O}(x) \).

We know from before, if we have \( \{q_i(0), p_i(0)\} \) and \( H \), then we can generate \( \{q_i(t), p_i(t)\} \) at any time \( t \) using \( F = m \dot{q}_i \), \( \ddot{q}_i = -\partial H / \partial p_i \), or alternatively \( \partial H / \partial q_i = -\dot{p}_i \), \( \partial H / \partial p_i = \dot{q}_i \).

If the system is "ergodic", then as \( t \to \infty \)
we will sample all configurations \( \{q(t), p(t)\} \) at \( H(p(t), q(t)) \) with equal prob, i.e. \( P(q, p) = P(p, q) = \sqrt{2 \pi \bar{N} \bar{v} \bar{e}} \)
so \( \langle \mathcal{O} \rangle = \int dp \int dq \mathcal{O}(p, q) \sqrt{2 \pi \bar{N} \bar{v} \bar{e}} \sqrt{2 \pi \bar{N} \bar{v} \bar{e}} \langle H(p, q) - \mathcal{E} \rangle \) / \( \sqrt{2 \pi \bar{N} \bar{v} \bar{e}} \)

\( \mathcal{R}(N, v, e) = \int dp \int dq \mathcal{S}(H(p, q) - \mathcal{E}) \) / \( \sqrt{2 \pi \bar{N} \bar{v} \bar{e}} \)

& it 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 rfg (gen vel from Boltermann dist)
2) interaction energy
Remember we previously said \( \frac{dA}{dt} = \Xi A, H^2 = \sum_{i=1}^{N} \left( \frac{dA}{d\phi_i} \frac{dA}{d\phi_i} + \frac{dA}{d\phi_i} \frac{dA}{d\phi_i} \right) \)

We can define \( i \mathcal{Y} A = \Xi H, A^3 \), \( i \mathcal{Y} = \Xi H, A^3 \phi(A) \)

so \( \frac{dA}{dt} = -i \mathcal{Y} A \)

formally \( A(t) = e^{-i \mathcal{Y} t} A(0) \), 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:

\[
\frac{\partial}{\partial t} \vec{q}(t+dt) \approx \dot{\vec{q}}(t) + d\vec{t} \frac{\partial \vec{q}}{\partial \vec{t}} \bigg|_{t+\Delta} - \frac{1}{2} d\vec{t}^2 \frac{d^2 \vec{q}}{d\vec{t}^2} \bigg|_{t+\Delta} + O(d^3 \vec{t})
\]

\[
\approx \dot{\vec{q}}(t) + d\vec{v} \vec{n}(t) + d\vec{v}^2 \vec{a}(t) \quad \text{[Remember:]} \quad \vec{d} = \Delta t \quad \vec{v}_0 + \vec{v}
\]

Remember \( a(t) = -\frac{2U(q(t))}{m} \cdot \frac{1}{m} = \frac{F}{m} \).

Also would need \( U(q(t+dt)) \), can do by finite diff:

\[
\vec{v}(t+dt) \approx \vec{v}(t) + \frac{\vec{v}(t+2\Delta t) - \vec{v}(t)}{2\Delta t} \quad \text{or by expanding}
\]

\[
\vec{v}(t+dt) \approx \vec{v}(t) + \Delta t \vec{a}(t) + O(d^2 \vec{t}^2), \quad \text{but people came up with schemes that are better.}
\]
Let's go back to formal description

\[
\frac{d\mathcal{P}}{dt} = -\frac{\partial H}{\partial q}, \quad \frac{dq}{dt} = \frac{\partial H}{\partial p}
\]

- \imath \mathbf{A} = \mathbf{S} \mathbf{H}, A^2 = \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}

\frac{dA}{dt} = \mathbf{S} \mathbf{A} \mathbf{H} \Rightarrow \mathbf{A}(t) = e^{t \mathbf{i}\mathbf{H}} \mathbf{A}(0)

Schemes to split i\mathbf{H}

Now, \( e^{A+B} \neq e^A e^B \) unless \([A,B] = AB - BA = 0\) and can show that \([i\mathbf{p}, i\mathbf{q}] \neq 0\) don't commute

Trotter Factorization

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