Molecular Dynamics Sims

Last time, discussed Monte Carlo Sims

⇒ Molecular dynamics is an alternative idea
Solve Newton's equations approximately, with the same idea of computing \( \langle A \rangle = \int \text{d}x \psi(x)|A(x)| \)

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

If the system is "ergodic", then as \( t \to \infty \)

will sample all configurations \( \mathcal{E} \mathcal{P}(e), \mathcal{q}(t) \rangle \) at \( \mathcal{H}(\mathcal{P}(e), \mathcal{q}(t)) \equiv \mathcal{E} \)

with equal prob, i.e \( \mathcal{P}(\mathcal{X}) = \mathcal{P}(\mathcal{P}(e), \mathcal{q}) = 1/\mathcal{S}(\mathcal{N}, \mathcal{V}, \mathcal{E}) \)

so \( \langle A \rangle = \int \mathcal{d}\mathcal{P} \int \mathcal{d}\mathcal{q} \mathcal{A}(\mathcal{P}, \mathcal{q}) S(\mathcal{H}(\mathcal{P}, \mathcal{q}) - \mathcal{E}) / \mathcal{S}(\mathcal{N}, \mathcal{V}, \mathcal{E}) \)

\( \mathcal{S}(\mathcal{N}, \mathcal{V}, \mathcal{E}) = \int \mathcal{d}\mathcal{P} \mathcal{d}\mathcal{q} S(\mathcal{H}(\mathcal{P}, \mathcal{q}) - \mathcal{E}) \)

& it ergodic \( \langle A \rangle = \lim_{T \to \infty} \frac{1}{T} \int_0^T \mathcal{d}t \mathcal{A}[\mathcal{P}(t), \mathcal{Q}(t)] \)

In practice: need: 1) initial starting config (generated from Boltzmann dist)
2) interaction energy
Remember we previously said \( \frac{dA}{dt} = \sum_{i=1}^{N} \left( \frac{\partial A}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial A}{\partial p_i} \frac{dp_i}{dt} \right) \)

and defined \( i_0^t \frac{dA}{dt} = \sum_{i=1}^{N} \frac{\partial A}{\partial q_i} \frac{dq_i}{dt} + \frac{\partial A}{\partial p_i} \frac{dp_i}{dt} \)

so \( \frac{dA}{dt} = i_0^t \frac{dA}{dt} \) so formally \( A(t) = e^{-i_0^t \frac{dA}{dt}} \), 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:

\[
\vec{q}(t+d\vec{r}) \approx \vec{q}(t) + d\vec{r} \frac{d^2\vec{q}}{dt^2} + \frac{d^2\vec{q}}{dt^2} \bigg|_{t=0} + O(d^3\vec{r})
\]

\[
\approx \vec{q}(t) + d\vec{r} \vec{v}(t) + \frac{d^2\vec{r}}{2} \alpha(t)
\]

Remember \( \alpha(t) = -\frac{\partial U(q(t))}{\partial q_i} \cdot \frac{1}{m_i} = F_i/m_i \)

Also would need \( U(t+d\vec{r}) \), can do by finite diff

\[
\frac{\vec{v}}{dt} = \frac{\vec{q}(t+d\vec{r}) - \vec{q}(t)}{d\vec{r}} \quad \text{or by expanding}
\]

\[
\frac{\vec{v}}{dt} \approx \vec{v}(t) + \frac{d\vec{r}}{dt} \vec{a}(t) + O(d^2\vec{r}) \]

but people came up with schemes that are better.
Example, could have written:

\[ \frac{d^2 \hat{\mathcal{V}}(t)}{dt^2} = \mathcal{V}(t) - \mathcal{V}(t_0) + \frac{d^2}{dt^2} \left[ \int_{t_0}^{t} \mathcal{V}(\tau) d\tau + \frac{1}{2} \mathcal{V}^2(t_0) \right] + O(d^3) \]

(add 1+2) \Rightarrow \frac{d^2 \hat{\mathcal{V}}(t)}{dt^2} = \frac{d^2}{dt^2} \left[ \mathcal{V}(t_0) - \mathcal{V}(t_0) \right] + \frac{d^2}{dt^2} \left[ \mathcal{V}(t) \right] = \mathcal{V}(t) - \mathcal{V}(t_0) + \frac{d^2}{dt^2} \mathcal{V}(t_0) \]

\[ \frac{d^2 \mathcal{V}(t)}{dt^2} = \left( \mathcal{V}(t_0) - \mathcal{V}(t) \right) / \mathcal{Z} \]

Verlet 1967, alternate these two eqns

Good idea to have time reversibility these equations are invariant under \( d \mathcal{Z} \rightarrow -d \mathcal{Z} \)

Another variant, using this backwards idea

\[ \mathcal{V}(t_0) - \mathcal{V}(t) \rightarrow -\mathcal{V}(t) + \mathcal{V}(t_0) \] (note \( v = \frac{d \mathcal{V}}{dt} \)

\[ -v = \frac{d \mathcal{V}}{dt} \rightarrow -v = \frac{d \mathcal{V}}{dt} \])

\[ \frac{d^2 \hat{\mathcal{V}}(t)}{dt^2} = \frac{d^2}{dt^2} \left[ \mathcal{V}(t_0) - \mathcal{V}(t) \right] = \frac{d^2}{dt^2} \left[ \mathcal{V}(t) \right] = \mathcal{V}(t) - \mathcal{V}(t_0) + \frac{d^2}{dt^2} \mathcal{V}(t_0) \]

Sub \( 1 \rightarrow 4 \rightarrow V(t_0) + \frac{d^2}{dt^2} \left[ F(t_0) + F(t) \right] \]

Alternate 1 & 5,

Let's go back to formal description

\[ \frac{d^2 Q}{dt^2} = -\frac{\partial H}{\partial Q} \quad \frac{d^2 P}{dt^2} = \frac{\partial H}{\partial P} \]

\[ -i \hbar \mathbf{A} = \mathbf{\Xi} H, \mathbf{A}^2 = \sum_{i=1}^{N} \frac{\partial H}{\partial Q_i} \frac{\partial}{\partial P_i} - \frac{\partial H}{\partial P_i} \frac{\partial}{\partial Q_i} \]

\[ dA/dt = \mathbf{\Xi} A/H_3 \implies A(t) = e^{t i \mathbf{\Xi} / H_3} \]

Can rewrite \( \mathcal{Y} = \mathcal{Y}_P + \mathcal{Y}_Q \) & analogous for \( N \) particles

\[ i \mathcal{Y}_P = -\frac{\partial H}{\partial Q} \quad i \mathcal{Y}_Q = -\frac{\partial H}{\partial P} \]

if \( H = \mathbf{P} \cdot \mathbf{m} + U \) \( \implies \)

\[ i \mathcal{Y}_P = -F \frac{\partial (mv)}{\partial x} \quad i \mathcal{Y}_Q = + \frac{m \mathbf{V}}{\partial \mathbf{Q}} \]

\[ \implies \]

\[ i \mathcal{Y}_Q = + v \frac{\partial \mathbf{P}}{\partial \mathbf{Q}} \]
Now, $e^{A+B} \neq e^A e^B$ unless $[A,B] = AB - BA = 0$ and can show that $[\pm i\gamma_p, \pm i\gamma_q] \neq 0$ don't commute.

**Trotter Factorization**

$$e^{A+B} = \lim_{P \to \infty} \left[ e^{A_1 P} e^{B_1 P} \cdots e^{A_P P} \right]^P$$

so

$$e^{i\lambda x} = \left[ e^{i\lambda x/2} e^{i\lambda x/2} + e^{i\lambda x/2} e^{-i\lambda x/2} \right]^M + O(M\Delta t^3)$$

(1 scheme)

Now $e^{c\frac{dx}{dt}} g(x) = g(x+c)$

Why?

$$g(x+c) = g(x) + \frac{c}{1!} g'(x) + \frac{c^2}{2!} g''(x) + \cdots = e^{c\frac{dx}{dt}} g(x)$$

Applying once to $A^0 = \varepsilon q_0, 0^0$, $P^0 = \varepsilon q_0, 0_0 + \frac{\varepsilon}{m} \Delta t^2/3$

$PAP = \varepsilon q_0 + \varepsilon \Delta t, 0_0 + \frac{\varepsilon}{m} \Delta t^2/3 = \varepsilon q_0 + \varepsilon v_0 + \frac{\varepsilon}{m} \Delta t^2, v_0$

$PAP = \varepsilon q_0 + \varepsilon v_0 + \frac{\varepsilon}{m} \Delta t^3, v_0 + \frac{\varepsilon}{2m} \Delta t^2$ again seems overly complicated, but this formulation allowed for many advanced methods to be derived using splitting schemes.
E.g. RESPA, evolve slow and fast forces

Separately, eg \( U^{\text{fast}} = U_{\text{spring}}(q) + U_{\text{other}}(q) \)

\[
& \dot{q}^\text{fast} = -F_{\text{fast}} \frac{d}{dp} + \dot{q}^\text{slow}, \\
& \dot{q}^\text{slow} = -F_{\text{slow}} \frac{d}{dp}
\]

Then can do

\[
\begin{align*}
& \exp \left[ i \tilde{\tau} \left( \begin{array}{c} \tilde{q}^\text{fast} \thinspace \tilde{p}^\text{fast} \\
& \tilde{q}^\text{slow} \thinspace \tilde{p}^\text{slow} 
\end{array} \right) \right] \\
& \approx \exp \left[ \begin{array}{c} i \tilde{\tau} \tilde{q}^\text{fast} \tilde{p}^\text{fast} \\
& + i \tilde{\tau} \tilde{q}^\text{slow} \tilde{p}^\text{slow} 
\end{array} \right]
\end{align*}
\]

Can save a lot of computer time if large range forces vary slowly.

Also, error in methods grow as \( \Delta t^{-2} \) or \( \Delta t^{-3} \), how small should \( \Delta t \) be. In practice, fit

Fastest motion in system, \( \omega = \sqrt{\kappa / \mu} \),

\[
\tau = \frac{\pi}{\omega}, \quad \text{want } \Delta t < \tau, \text{ maybe } \Delta t < \tau / 5
\]

C-H bond \( \tau < 0.05 \text{ fs} \), so MD sim \( \Delta t \sim 0.5 \text{ fs} \)

w/ rigid CH ...
Enhanced Sampling

We said before that the time avg
\[
\langle A \rangle = \lim_{N \to \infty} \frac{1}{N} \sum_{i=1}^{N} A(X_i)
\]
for N mc samples

or \( N = T/\Delta t \) and time steps is true if
the system is ergodic, i.e. sees all the stats.

The problem in real simulation is \( N \neq 0 \),
\( N \sim (1 - 10^{10}) \).

This works for some problems, but there
is a very common problem.

Suppose \( U(x) \)
\[ \text{or } F(A) \]
\[ \text{or } \mu, \Delta F \]

\[ F(x) = -kT \log \int S(M(\frac{\mu}{kT}) - \frac{\mu}{kT}) e^{-\beta U(x)} dx - F_0 \]
(Potential of mean force)

Rate \( A \to B \) \( \propto e^{-\beta A \mu} \) or \( e^{-\beta A \Delta F} \)

So if \( \text{rate} >> N \Delta t \), then you will
be trapped in \( A \) (or \( B \))
(rare event problem)

We need tricks to overcome this problem!